Materials Science and Engineering A 540 (2012) 1–12

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Review

Grain boundaries in ultrafine grained materials processed by severe plastic deformation and related phenomena☆

X. Sauvage[a,*], G. Wilde[b], S.V. Divinski[b], Z. Horita[c], R.Z. Valiev[d,**]

[a] University of Rouen, CNRS UMR 6634, Groupe de Physique des Matériaux, Faculté des Sciences, BP12, 76801 Saint-Etienne du Rouvray, France
[b] Institute of Materials Physics, University of Münster, Münster, Germany
[c] Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan
[d] Institute for Physics of Advanced Materials, Ufa State Aviation Technical University, K. Marx 12, Ufa 450000, Russia

ARTICLE INFO

Article history:
Received 28 October 2011
Received in revised form 20 January 2012
Accepted 21 January 2012
Available online 28 January 2012

Keywords:
SPD
UFG
Grain boundary
Grain boundary segregation
Grain boundary diffusion

ABSTRACT

Grain boundaries in ultrafine grained (UFG) materials processed by severe plastic deformation (SPD) are often called "non-equilibrium" grain boundaries. Such boundaries are characterized by excess grain boundary energy, presence of long range elastic stresses and enhanced free volumes. These features and related phenomena (diffusion, segregation, etc.) have been the object of intense studies and the obtained results provide convincing evidence of the importance of a non-equilibrium state of high angle grain boundaries for UFG materials with unusual properties. The aims of the present paper are first to give a short overview of this research field and then to consider tangled, yet unclear issues and outline the ways of oncoming studies. A special emphasis is given on the specific structure of grain boundaries in ultrafine grained materials processed by SPD, on grain boundary segregation, on interfacial mixing linked to heterophase boundaries and on grain boundary diffusion. The connection between these unique features and the mechanical properties or the thermal stability of the ultrafine grained alloys is also discussed.

Contents

1. Introduction

With grain sizes in a submicron (100–1000 nm) or nanocrystalline (<100 nm) range ultrafine-grained (UFG) materials contain in their microstructure a very high density of grain boundaries (GBs), which can play a significant role in the development and exhibition of novel properties. For this reason, UFG materials can be typically considered as interface-controlled materials [1]. Unlikely to the nanocrystalline materials where grain boundary material can represent a significant, e.g. a percent or even larger fraction of the whole volume, the volume fraction of GBs in an UFG material is less than 1%. However, the structure, kinetic and thermodynamic properties of GBs could be modified so significantly that they start to dominate some important material properties.

Already in first works on nanocrystalline materials pioneered by Gleiter and colleagues it was suggested that grain boundaries can possess a number of peculiar features in terms of their atomic structure in contrast to grain boundaries in conventional polycrystalline materials [1,2]. Further studies delivered plenty of indications towards this idea, evidencing simultaneously the fact that solely

☆ At the invitation of the MSE A editors, the winner of the 2011 Materials Science and Engineering: A prize, Professor Rusian Z. Valiev has contributed this paper co-authored by X. Sauvage, G. Wilde, S.V. Divinski and Z. Horita, which considers the nature of grain boundaries in alloys subjected to severe plastic deformation. MSE A editors and staff all want to again congratulate Prof. Valiev and thank him for submission of this manuscript.

* Corresponding author. Tel.: +33 2 32 95 51 42; fax: +33 2 32 95 50 32.
** Corresponding author. Tel.: +7 3472 233422; fax: +7 3472 233422.
E-mail addresses: xavier.sauvage@univ-rouen.fr (X. Sauvage), rzvaliev@mail.rb.ru (R.Z. Valiev).

0921-5093/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2012.01.080

the grain size is not the deciding parameter. For example, specific grain boundaries were revealed in ultrafine-grained materials produced by severe plastic deformation (SPD) techniques [3]. In the recent decade the use of SPD techniques for grain refinement and nanostructuring of metals and alloys attracted intensive attention and received much development due to their possibility not only to enhance properties of different materials but also to produce mulifunctionality of the materials including commercial alloys and composites and presently, these developments witness the stage of transition from laboratory research to their practical application [4–6].

Depending on the regimes of SPD processing different types of grain boundaries can be formed in the UFG materials (high- and low-angle, special and random, equilibrium and so-called "non-equilibrium" grain boundaries) [3,7], which paves the way to grain boundary engineering of UFG materials, i.e. to the control of their properties by means of varying the grain boundary structure. For example, recent studies demonstrated that transport properties of UFG materials (diffusion, segregation, etc.) are markedly affected by a so-called "non-equilibrium" grain boundary state [8–10]. At this place it is important to highlight that a broad spectrum of diffusivities of short-circuit paths is observed in UFG materials—contributions of high-angle grain boundaries with both "normal" and significantly enhanced diffusion rates can be differentiated in SPD-processed materials [11,12]. In this context, the "normal" diffusion rates are those which reveal the relaxed general high-angle grain boundaries as they are present in well-annealed polycrystalline counterparts[1] and the non-equilibrium interfaces are characterized by considerably higher diffusion coefficients. This hierarchy of interfaces in terms of their corresponding diffusivities is proposed [12] to explain the apparent contradictions between earlier publications that reported either conventional or unusual properties for grain boundaries in nanocrystalline or ultrafine grained materials.

The notions on non-equilibrium grain boundaries were first introduced in the scientific literature in the 1980s [13,14] reasoning from investigations of interactions of lattice dislocations with grain boundaries. According to [14] the formation of a non-equilibrium grain boundary state is characterized by three main features, namely, excess grain boundary energy (at the specified crystallographic parameters of the boundary), the presence of long range elastic stresses (Fig. 1) and enhanced free volume. Discontinuous distortions of crystallographically ordered structures, that may come about by accommodation problems of differently oriented crystallites of finite sizes or by high densities of lattice dislocations and their interaction with grain boundaries can be considered as sources of elastic stress fields that modify the atomic structure of high angle grain boundaries so that their excess free energy becomes enhanced. Somewhat unfortunately, these "unusual" grain boundaries have been termed "non-equilibrium" grain boundaries although in a strict sense, each grain boundary is a non-equilibrium defect if segregation effects (see Section 3) are not to be considered. Since however the term has been accepted and utilized by the entire community who works on severe plastic deformation, we will also use it here.

A model for these non-equilibrium grain boundaries has been developed by Nazarov, Romanov and Valiev in a series of papers [15,16] describing their formation. Lattice dislocations that are created during the plastic straining move towards high angle grain boundaries on their respective glide planes during continued straining and then, when reaching a high-angle grain boundary, transform into so-called "extrinsic grain boundary dislocations", i.e. dislocations that do not contribute towards the misorientation of the two adjacent grains. As a net effect, high angle grain boundaries with high densities of such extrinsic grain boundary dislocations would also contain increased energy and free volume and considerable microstrain associated with the grain boundary region [15].

In recent years the non-equilibrium grain boundaries in UFG materials and related phenomena (diffusion, segregation, etc.) have been the object of intense studies performed by the authors of this paper and the obtained results provide convincing evidence of the importance of a non-equilibrium state of high angle grain boundaries for UFG materials with unusual properties. At the same time the complexity of such research becomes evident, involving the most contemporary techniques of structural analysis and, occasionally, different interpretation of the obtained results. All this specifies the aims of the present paper—first, to introduce the readers to this research field of recent studies of grain boundaries in bulk nanostructured materials where unique features about their structures and properties are outlined; second, to consider tangled, yet unclear issues and outline the ways of oncoming studies. The available models of the "non-equilibrium" GBs will be examined against the newest experimental data.

2. Structure of grain boundaries in ultrafine grained materials

The atomistic structure of random high-angle grain boundaries has been discussed since several decades by different models assuming quite different structural arrangements ranging from an amorphous structure to local structural units with high packing densities that are arranged non-periodically along the boundary plane, see, e.g. [17–19], to mention just a few examples. In recent years, atomistic simulations have considerably contributed to the understanding of grain boundary structures [20–23], yet without yielding a unique description of the atomic structure of random high angle grain boundaries.

However, the goal set for the present review is not to unravel the real space arrangement of atoms within the boundary plane of random high angle grain boundaries, but analyse the structural modifications of high angle grain boundaries inflicted by severe plastic deformation processing, for formation of which during SPD processing exist already strong indications, see, e.g. [3,24]. In earlier studies of grain boundaries in UFG materials processed by SPD techniques there have been already used various, often mutually complementary, structural methods: transmission electron microscopy (TEM), X-ray diffraction, Mössbauer spectroscopy, dilatometry, differential calorimetry and others (see, e.g. [3]). They clearly evidenced that mostly high-angle grain boundaries leading to grain refinement can be formed after optimization of SPD processing routes and these grain boundaries possess specific non-equilibrium structures. Later, structure sensitive probes have been applied that are sensitive to modifications of the atomic structure, such as grain boundary diffusion measurements (see Section 5) or high resolution transmission electron microscopy (HRTEM) analyses, in order to identify and characterize transformations of the grain boundary structure due to the severe deformation processing.

Horita et al. [24] as well as Valiev et al. [3] noticed serrated contrast features in bright field transmission electron microscopy (TEM) images and also in HRTEM analyses, respectively that were interpreted as evidence for a high local density of dislocation structures associated with the apparent non-equilibrium grain boundary. However, due to the possible Moiré effect occurring in the projection of sample regions near interfaces and due to the

[1] Where they are typically the fastest short-circuit diffusion paths.