J Mater Sci (2011) 46:4095–4115
DOI 10.1007/s10853-011-5393-z

IIB 2010

Grain boundary engineering: historical perspective and future prospects

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Received: 10 September 2010 / Accepted: 12 February 2011 / Published online: 1 March 2011

Abstract A brief introduction of the historical background of grain boundary engineering for structural and functional polycrystalline materials is presented herewith. It has been emphasized that the accumulation of fundamental knowledge about the structure and properties of grain boundaries and interfaces has been extensively done by many researchers during the past one century. A new approach in terms of the concept of grain boundary and interface engineering is discussed for the design and development of high performance materials with desirable bulk properties. Recent advancements based on these concepts clearly demonstrate the high potential and general applicability of grain boundary engineering for various kinds of structural and functional materials. Future prospects of the grain boundary and interface engineering have been outlined, hoping that a new dimension will emerge pertaining to the discovery of new materials and the generation of a new property originating from the presence of grain boundaries and interfaces in advanced polycrystalline materials.

Introduction

During the past century, our knowledge of interfaces, i.e., grain boundaries and interphase boundaries in crystalline solids has enormously developed from a tiny seed to a huge tree with many branches. Since 1880s, when Sorby first showed the optical micrographs of a blister steel to demonstrate the presence of large number of grains with various shapes and sizes and the boundaries between the adjoining grains [1], grain boundaries and interphase boundaries have drawn an increasing attention of materials scientists and engineers who are deeply involved in materials design and development. It has now been well established that the microstructure is closely related to bulk properties of materials. Accordingly, the control of microstructures has become one of the key issues of the discipline of Physical Metallurgy (earlier) and Materials Science and Engineering (modern). Till date, a large variety of approaches for microstructural control in polycrystalline materials have been attempted by using the available processing methods. These methods include different metallurgical processes such as solidification, alloying and thermo-mechanical processing. Much effort has been made to develop a more powerful and efficient processing method than the conventional ones. There is always a quest to produce such well engineered microstructures that can confer desirable bulk properties, mostly in polycrystalline materials, except the case of semiconductors like silicon which are generally single crystalline, as required by the technological applications.

Amongst the past achievements pertaining to the development of newer processing methods, rapid-solidification, directional solidification, and zone-melting have been developed in the case of solidification processing. These techniques as well as some other recently developed ones are widely utilized as powerful processing methods of microstructure control [2–4]. In the past three decades, a number of new techniques for materials processing have been developed and some of them have been successfully applied to the production of advanced metallic, semiconductor, and ceramic materials by tailoring desirable and stable microstructures [5]. Amongst these the processing methods, processing under magnetic [6, 7] and electric fields [8] are noteworthy.

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On the occasion of the iib2010, it may be useful to briefly summarize the previous studies which played important roles in the historical development of interface science, and to re-affirm the established concepts. It is also imperative to mention what needs to be studied further in order to strengthen the new discipline of Interface Engineering for polycrystalline materials with desirable bulk properties and high performance. In the past three decades, the grain boundary and interface engineering has been extensively attempted with basic knowledge of grain boundaries and interfaces, to improve bulk properties and performance of conventional materials. Moreover, grain boundary and interface engineering may have potential to impact a new property and hence, new functions for future advanced materials. The present author believes that a brief review of important studies of grain boundary-related properties may be useful for the new comers to know the background as well as the recent achievements, and also to specify the milestones leading to the future of Interface Engineering.

As discussed by Swalin almost 40 years ago [9], the development of science is generally considered to pass four phases following an S-curve: (i) the first "Conceptual phase", is the era when nothing is really known about the subject. General philosophical principles, that are involved to explain observations, grow very slowly in this phase. (ii) Then comes the "Discovery phase", which is a period of rapid acceleration. Discoveries are unexpected and thought provoking. In this phase, numerous but conflicting theories are proposed. The research field seems to be full of puzzles. Many highly motivated scientists enter the field with a hope to achieve notable accomplishments. (iii) The third phase is known as "Breakthrough phase". In this phase, the field makes a rapid progress and becomes fashionable in the leading laboratories. The general pattern of scientific events is understood. The field is exciting and rewarding. (iv) Ultimately, "Classical phase" sets in, where the remaining pieces of the jigsaw are put in place. The thought patterns generalized in the breakthrough phase become orthodox and become the conventional wisdom which must be broken through in the next major advance ultimately leveling off until a new breakthrough occurs. In my personal opinion, the field of grain boundary and interfaces is now passing through the "Breakthrough phase" experiencing a rapid advancement. Accordingly, the time is ripe for a number of new challenging tasks with adequate theoretical and experimental tools.

Development of physical metallurgy to interface science in the twentieth century

Since 1880s, when metallographic observation of iron and steels was first made by Sorby [1], microstructural aspects have become key to Physical Metallurgy which transformed to Materials Science and Engineering (MSE) after 1960s, as reviewed by R. F. Mehl [10] and R. W. Cahn [11]. A systematic study of the evolution of microstructure in polycrystalline materials composed of a large variety of grain structures was carefully performed by C. S. Smith in 1940s, to find the key factors controlling grain growth, paying particular attention to grain boundaries in single phase materials and also inter-phase boundaries in multi-phase alloys [12]. Based on his elaborate effort pertaining to experimental observations, it has been revealed that the interface energy plays a key role in the evolution of microstructure in polycrystalline materials. In 1950s, probably K.T. Aust and B. Chalmers were amongst the first who seriously discussed the relation between energy and structure of grain boundaries [13]. The structure of grain boundaries was first investigated theoretically by Read and Shockley on the basis of dislocation theory [14, 15]. On the other hand, optical microscopy of grain boundaries was attempted by Amelinckx through the observation of particle decorating boundaries in transparent crystals such as NaCl for low-angle dislocation boundaries [16]. Hirsch et al. [17] applied transmission electron microscopy (TEM) for the observations of dislocation boundaries in deformed aluminum for the first time.

The first book on the topic of the structure and properties of grain boundaries and boundary-related phenomena in polycrystalline materials was written by Donald Mclean in 1957 [18]. Almost 30 years later, in 1995, Sutton and Balluffi published their excellent book entitled "Interfaces in Crystalline Materials" [19]. The period between 1960s and 1980s can be recognized as the first half of the breakthrough phase in the history of research on grain boundaries and interfaces. During this period, a number of new concepts on grain boundary structure have been proposed on the basis of computer simulation and systematic experimental studies with orientation-controlled bicrystal samples, exploring grain boundary structure–property relationship. After 1990s, experimental study of the structure–property relationship of grain boundaries have become possible for polycrystalline samples, because a computer-assisted and fully automated technique for orientation determination and boundary characterization Scanning Electron Microscopy based Electron Back Scatter Diffraction (SEM-EBSD)/Orientation-Imaging Microscopy (OIM) was developed by Adams et al. in the early 1990s [20, 21]. Subsequently, the characterization of grain boundary microstructure by SEM-EBSD/OIM has become a standard method for precise and quantitative analysis of the microstructure in polycrystalline samples of metallic, semiconductor, and ceramic materials with different crystal structures and a wide range of grain sizes (from a few 100 μm to nanocrystalline range). It is now possible to

characterize samples with grain size down to a few 10 nm with the use of a Field Emission Gun-Scanning Electron Microscope with orientation imaging microscopy facility (FEG-SEM/OIM) [22].

Table 1 is a tentative list of important achievements in the research field of grain boundaries and interfaces in crystalline solids during the past almost one century. From this table, one can recognize that the period of 1900s–1950s may correspond to "Conceptual Phase" of scientific development of Interface Science. The next period from 1960s to 1980s may correspond to "Discovery Phase" in which a number of new experimental techniques for the observation of structure of grain boundaries and interfaces were developed. The relation between structure and properties of grain boundaries were systematically and carefully studied by using orientation-controlled bicrystals of metals and alloys. In particular, the advent of electron microscopy and its further development to high resolution transmission microscopy (HREM) greatly contributed to experimental verification of the basic concepts of the atomic structures of grain and phase boundaries, both previously stated and newly proposed. During this period, the scope of research on polycrystalline materials greatly widened from the simplest case of bicrystal with a single boundary to the extreme case of nanocrystalline materials which are characterized by extremely high volume fraction of grain boundaries, sometimes more than 50% of that of the material, as discovered by Gleiter et al. [23]. The advent of nanostructured materials opened a new domain in which structure and properties of crystalline interface need to be studied more fundamentally in the light of atomic bonding at crystalline interfaces. The development and usage of a high performance computer greatly enhanced the progress in Interface Science of crystalline solids.

The possibility of a new approach to "Grain Boundary Engineering (GBE)", initially called "Grain Boundary Design and Control" was proposed by the present author in the early 1980s [24] to confer desirable bulk properties and high performance to polycrystalline materials. Aust and Palumbo [25] have first applied this concept to improve bulk mechanical and fracture properties in structural materials, such as materials for nuclear applications that require high-resistance to stress corrosion cracking. More recently the grain boundary engineering has been applied

Table 1 A brief history of research field of structure and properties of grain boundaries, interfaces and related fields during the past one century

1900s–1940s
Amorphous Cement Theory (Rosenhain-Ewen, 1912)
Coincidence-Site-Lattice (CSL) Model (G. Friedel 1920, Kronberg-Wilson 1949)
Transition-Lattice Theory (Hargreaves-Hill, 1929)
Geometrical and Topological Approach to GB microstructure (C. S. Smith, 1948)
1950s–1960s
Dislocation Theory of Low-angle GBs (Read-Shockley, 1952, Amelincks. 1957)
Boundary Structure and Properties in Bicrystals (Chalmers-Aust, R. W. Cahn)
Thermodynamics of GBs (J. W. Cahn. 1956), First Book on GBs (D. McLean, 1957)
Geometrical and Mathematical Approach to CSL (Brandon, Ranganathan. 1966)
FIM, TEM Observations (Brandon, Ryan-Suiter, Smith, Ralph-Jones, Gleiter)
O-Lattice Theory (Bollmann, 1968)
1970s–1980s
HREM of GB Structure (Schober-Balluffi-Bristowe, Sass-Carter, Smith-Pond-King, Ishida-Ichinose, Bourret-Bacman, Rühle)
Bicrystal Work in Metals (extensively in France, Russia, Japan)
Extension of CSL. model to HCP. Non-cubic crystals (Bruggemen-Bishop, Grimmer-Warrington)
Computer Calculations (Biscondi, Vitek-Sutton. Wolf, Doyama-Kohyama)
Nanocrystalline Materials (Gleiter)
Interface in Phase Transformation (Hillert, Aaronson-Enomoto-Purdy, Maki-Furuhara)
1990s–2000s
Microscale Texture Analysis (Lücke-Gottstein, Bunge-Esling)
SEM-EBSD/OIM (Dingley-Adams-Wright-Kunze, 1991–1993)
GB Microstructure & Properties in Polycrystalline Materials (Aust-Palumbo-Erb, Ralph-Howell-Jones-Randle, Grabski, Priester, Watanabe-Kokawa-Tsurekawa)
Bicrystal Berhaviour (Metals: Gottstein-Shvindllerman-Straumal-Molodov-Winning, Paidar-Lejcek, Miura-Hashimoto-Mimaki, Mori-Monzen-Kato-Miura, Ceramics: Sakuma-Ikuhara- Yoshida-Yamamoto-Shibata)
Triple-Junction Behavior (Gottstein-Shvindlerman, King, Aust-Palumbo)
Nanocrystalline Materials by ECAP Processing (Valiev-Langdon-Nemoto-Horita)

to functional materials. Probably, past 1990s, Interface Science and Engineering is passing through the "Breakthrough phase". A number of new experimental techniques are available for the observation and characterization of interfacial structure and properties. Theoretical basis has now been reasonably established for complete understanding of the observations pertaining to the structure and properties of crystalline interfaces. However, there is a strong demand for experimental and theoretical basis for future study of statistical and topological features of interfacial microstructure and related properties in single- and multi-phase polycrystalline materials, with the grain sizes ranging over three orders of magnitude from conventional micrometer size to nanometer size. A rapid progress in "Interface Science and Engineering" can be expected, particularly in the area of advanced functional materials such as semiconductors and electroceramics where there is a strong need for the control of interfaces and also there is a high potential for creation of a new function associated with interfaces, as predicted by Interface Engineering.

The origin of the heterogeneity of grain boundary phenomena

As a fundamental understanding, it is a common recognition that grain boundary phenomena can occur very differently from boundary to boundary in a polycrystalline material. From Fig. 1, it is evident that most of the grain boundary phenomena occur very heterogeneously. Some examples are the intergranular fracture in Bi-doped copper (Fig. 1a, b) [24], the intergranular corrosion in iron–chromium alloy (Fig. 1c), and the dynamic grain boundary migration in aluminum under cyclic loading at high temperature (Fig. 1d) [26]. The activity of individual grain boundaries varies greatly amongst themselves, for example, some boundaries tend to break, corrode, and migrate easily, while some others show only a little or no activity. In fact, such heterogeneity and different local behavior of grain boundary phenomena can be appreciated by careful microscopic observations in polycrystalline materials. Of course, we know that the presence of grain boundaries is the primary origin of microstructural difference between a single crystal and a polycrystal. Accordingly, the microstructure in polycrystal can greatly vary depending on grain shape, grain size, the dimension of specimen (1D—wire, 2D—thin film, 3D—bulk), and geometrical configurations of grain boundaries.

Moreover, there is another important origin of the heterogeneous occurrence of grain boundary phenomena that is the effect of grain boundary structure and character. In the last five decades, much effort has been made to establish the relation between grain boundary structure and properties, particularly by using bicrystal samples of metals and alloys. It is now well established that grain boundary properties strongly depend on the grain boundary structure and character defined at least by the misorientation relationship between adjacent grains: crystallographic orientation of the rotation axis, the misorientation angle and the boundary inclination, using five geometrical parameters [19]. It is our current understanding that the activity of grain boundary phenomena can vary, depending on grain boundary structure and character, as much as one order of magnitude. Furthermore, the grain boundary microstructure which is defined by the grain boundary character distribution (GBCD), geometrical configurations of boundaries and other factors [24], can be modified and controlled by the processing method and conditions in polycrystalline materials. Thus, structure-dependent boundary properties are the possible origin of the heterogeneity of grain boundary phenomena decisively controlling bulk properties and performance of polycrystalline materials. Recent studies of grain boundary microstructures in polycrystalline

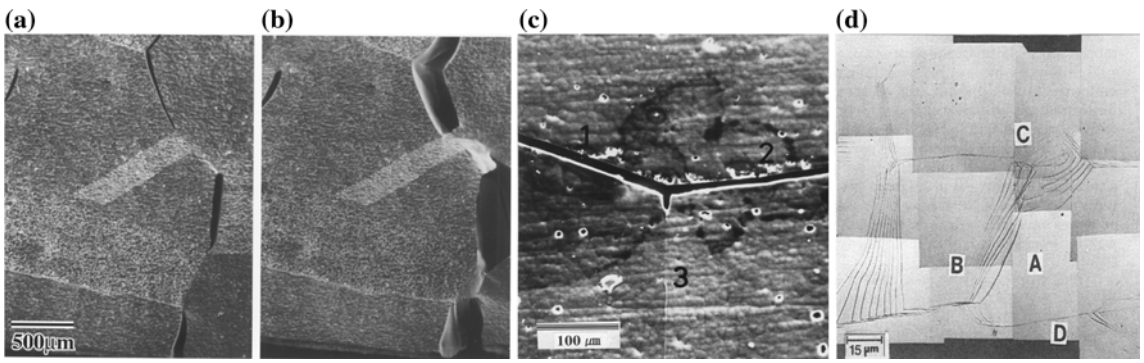

Fig. 1 The heterogeneity of grain boundary phenomena observed in metallic polycrystalline materials: **a**, **b** structure-dependent grain boundary fracture in Bi-doped copper [24]. Note that twin boundaries are a strong barrier to the propagation of intergranular crack, **c** different propensities to intergranular corrosion for the three boundaries meeting at a triple junction in Fe–16%Cr alloy, **d** structure-dependent dynamic migration during cyclic deformation in aluminum at high temperature [26]

materials (mostly metallic) have revealed to what extent the processing method and condition can affect the grain boundary microstructures in real engineering materials. Grain Boundary and Interface Engineering has just reached the stage of contributing to the practical applications in order to develop advanced materials with desirable bulk properties and high performance, after the "Breakthrough phase", based on the basic knowledge of structure-dependent boundary properties in bicrystals, as shown in the next section.

Importance of basic knowledge of structure-dependent properties in bicrystals

It was realized since 1950s that in order to understand and effectively utilize the influence of grain boundaries on bulk properties in polycrystalline materials, a basic study of the relationship between structure and properties was inevitably required [27]. A considerable effort has been made toward the study of structure-dependent grain boundary properties by using orientation-controlled bicrystals of metals and alloys, as documented in the classical reviews by Weinberg [28], Goux [29], Gleiter and Chalmers [30], Pande and Chou [31]. More recently, systematic and quantitative experimental studies on bicrystals have been performed for refractory metals such as niobium [32], molybdenum [33], non-oxide ceramics [34], oxide ceramics [35], and the intermetallics Ni_3Al [36]. In the past, there were difficulties in the preparation for bicrystals of these materials. However, with the advent of new crystal growing techniques, it is now possible to prepare bicrystals of a variety of materials. In addition to a number of previous studies, these techniques have greatly contributed to the recent progress and establishment of the discipline of Materials Interface Science, as reported in the conference proceedings series, particularly of the iib-conferences [37–39]. A more detailed account of the relationship between structure and properties of crystalline interfaces can be obtained from excellent books on this topic [30, 40–42].

Figure 2a shows the HREM micrographs of the atomic structures of grain boundaries. The misorientation dependence of the grain boundary energy for the ⟨110⟩ symmetric tilt boundaries in zirconia ZrO_2 bicrystals as experimentally determined by Shibata et al. [43] is presented in Fig. 2b. It is evident that the 5° low-angle dislocation boundary and low-Σ (3, 9, 11) coincidence boundaries possess periodic structures and lower values of the grain boundary energy. On the other hand, high-angle random boundaries without any special misorientation tend to possess higher grain boundary energies. The observations provide a direct evidence for structure-dependent grain boundary property without any ambiguity. Furthermore, the application of Electron Energy Loss Spectroscopy (EELS) and Energy Loss Near Edge Structures (ELNES) with far better energy resolution provide very detailed information on the nature of inter-atomic bonds across grain boundaries in ceramics [43]. Such data on structure-dependent boundary properties have been extensively accumulated in the past half century and time is ripe

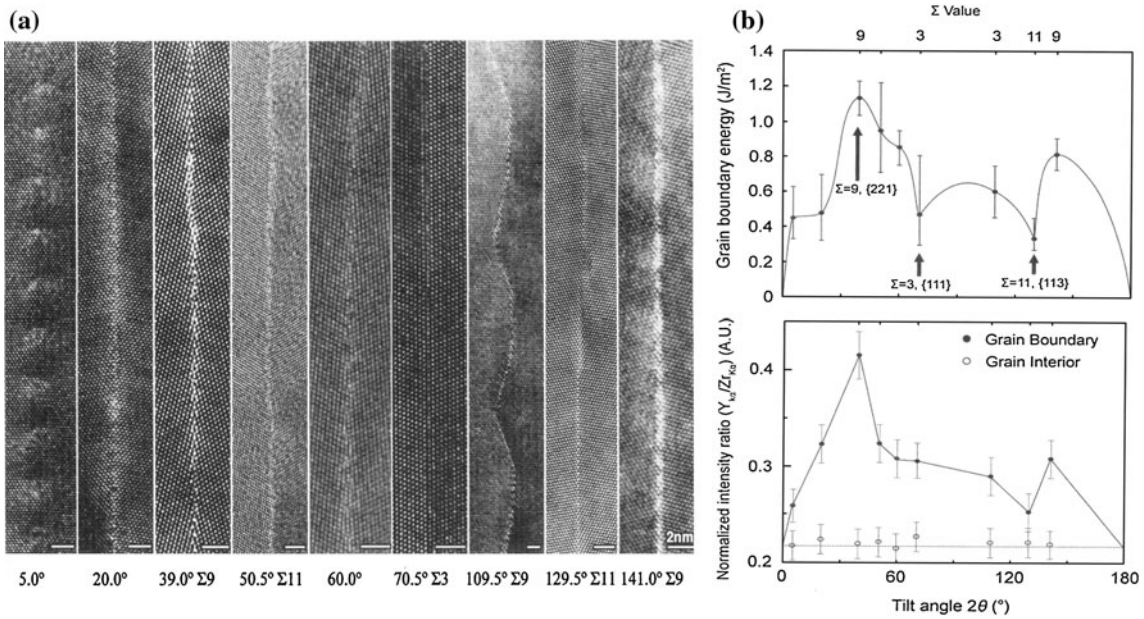

Fig. 2 **a** HRTEM images of symmetric tilt grain boundaries in zirconia bicrystals, **b** the misoreintation dependence of the grain boundary energy (*top*) and the misorientation dependence of Y segregation at symmetric tilt grain boundaries in Y-stabilized zirconia bicrystals [43]

for materials design and development on the basis of newly established concepts of grain boundary engineering and interface engineering.

A typical feature of structure-dependent grain boundaries obtained from quantitative experimental studies on bicrystals is schematically shown in Fig. 3. The magnitude of the activity or the extent of occurrence is given as a function of the misorientation angle for specific grain boundary phenomena concerned: diffusion, migration, sliding, corrosion, segregation, precipitation, fracture, even for electrical activity in semiconductor and superconductor. Here, one can simply differentiate the structure-dependent grain boundary properties into two types: Type A (shown on the top) and Type-B (shown on the bottom), as a function of the misorientation angle. Type-A curve describes the structure-dependent activity of higher-energy boundaries so that the higher energy boundaries show more dominant properties. On the other hand, Type B curve describes the structure-dependent properties of typical lower-angle/low-energy boundaries and special high-angle boundaries/low-energy special boundaries around a cusp corresponding to low-Σ coincidence orientations. Low-energy boundaries show more structure-sensitive nature of boundary properties, such as fracture strength. It is not difficult to understand such a generalized feature of structure-dependent boundary properties, because the activity of grain boundary can be influenced by the grain boundary energy which is also a structure-dependent boundary property [24]. Accordingly, the grain boundary energy can directly or indirectly affect the activity of grain boundary phenomena so that such a phenomenon can take place more dominantly at higher-energy boundaries. On the other hand a stronger resistance to grain boundary phenomena can be observed at grain boundaries with lower energy. This is the primary reason why grain boundary character distribution (GBCD) and grain boundary connectivity play a key role in controlling grain boundary-related bulk properties in polycrystalline material. However, we also need to consider the effect of the boundary inclination on its properties. This is particularly important for Σ3 coincidence boundary, the so called twin boundary, wherein, there is a significant difference in the boundary properties between coherent and incoherent twin boundaries due to the difference in boundary inclination.

Σ Dependence of properties of coincidence boundaries

There is a long pending dispute amongst grain boundary researchers concerning the utility of well-known parameter Σ which has been generally used to characterize special grain boundaries depending on the size of the unit cell of superlattice or the degree of structural order of grain boundaries in terms of the Coincidence-Site-Lattice (CSL) model, comprehensively explained by Balluffi [44]. It is assumed that the degree of structural order of CSL boundaries (simply termed as "coincidence boundaries") decreases with increasing the value of Σ. This suggests that low-Σ coincidence boundaries must have special properties such as low boundary energy compared to the high-angle/random boundaries with Σ value larger than 29 [45]. However, some researchers insist that observed grain boundary properties cannot be uniquely related to Σ in

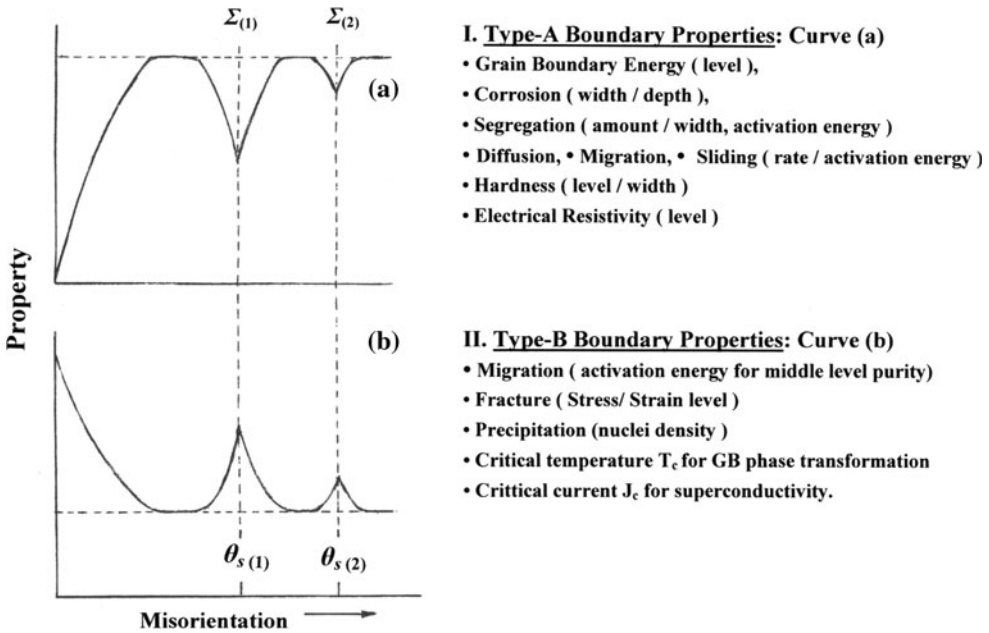

Fig. 3 Classification of structure-dependent grain boundary properties: Type-A boundary properties show more significant behavior at higher energy boundaries, while Type-B boundary properties show the opposite behavior, being more significant at lower-energy boundaries, particularly at low-Σ coincidence boundaries with a special misorientation angle θ_s

descending or ascending order of its number, because Σ does not have any physical significance with regards to the grain boundary inclination which is an important geometrical factor to define the character of grain boundary.

The author would like to express his personal view on the above mentioned argument. First, let us consider the reason why such a dispute was raised and is still debated. One of possible reason could be due to the fact that the basic studies of structure-dependent boundary properties have been often performed for FCC metals, particularly copper and its alloys with low-stacking fault energy, where twin boundaries can occur preferentially. In fact, Smith [46] has shown that there is a salient difference in Σ dependence of the area-density of coincidence sites σ between FCC and BCC coincidence boundaries. As shown in Fig. 4, the area density of coincidence sites σ for FCC coincidence boundaries is not uniquely related to Σ, showing the occurrence of three different groups for the relation between the area density σ and volume density Σ. The group of coincidence boundaries with Σ given by $\Sigma = 8n - 1$ ($n \geq 1$), i.e., Σ7, Σ15, Σ23, in terms of present author's description, shows the highest level of σ on the σ vs. Σ curve. The group with Σ given by $\Sigma = 8n - 5$ ($n \geq 1$), i.e., Σ3, Σ11, Σ19, Σ27 come to the lowest level of the σ vs. Σ curve. The group given by $\Sigma = 8n - 3$ or $\Sigma = 8n + 1$ ($n \geq 1$) lies between the above two groups. On the other hand, in the case of BCC crystal, the area density σ is uniquely related to Σ for all coincidence boundaries following a single curve. The prediction by Smith has brought about an important finding that the structure-dependent boundary properties of FCC coincidence boundaries do not simply depend on Σ (of the order of Σ value), but those of BCC coincidence boundaries do. In fact, the above hypothesis has been supported by experimental studies of the grain boundary character distribution in rapidly solidified and annealed ribbons of iron–6.5%slicon alloy with BCC structure and a sharp ⟨100⟩ or ⟨110⟩ texture [45, 47]. As shown in Fig. 5a for the ⟨110⟩ textured ribbon sample, those coincidence boundaries which occur more frequently are Σ1, Σ3, Σ9, Σ11,

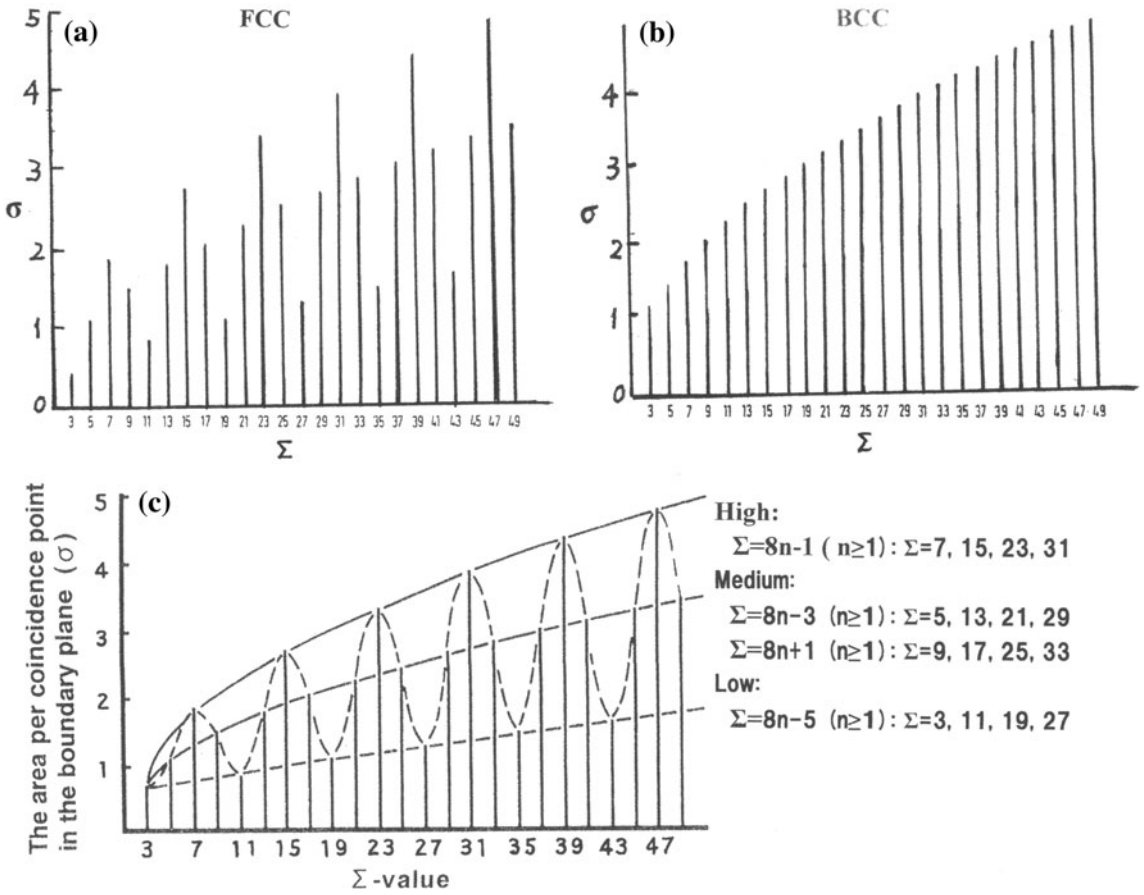

Fig. 4 The minimum area in the twin plane per coincidence site as a function of Σ (<50) for the FCC lattice and the BCC lattice, taking a lattice parameter of unity and with the ordinate in units of $Å^2$. After D. A. Smith [46] (*upper figures*) and a schematic illustration of three different groups of coincidence boundaries in FCC crystals originally reported in [49] and partly revised by the author (*bottom figure*)

Σ17, Σ19 boundaries in ascending order of Σ value as exactly predicted from the coincidence orientations for ⟨110⟩ rotation axis. Furthermore, by using the same ⟨110⟩ textured Fe–6.5mass%Si alloy ribbon samples, the relative grain boundary energy was determined by the dihedral-angle measurement technique [48]. The observed misorientation dependence of the relative boundary energy is shown in Fig. 5b. It is evident that low-angle (Σ1) boundaries with misorientation smaller, ca. 10° and low-Σ coincidence boundaries with Σ3 and Σ9 coincidence orientations possess much lower relative boundary energies than random general boundaries. A slight difference of the observed relative boundary energies for Σ3 and Σ9 coincidence boundaries at different misorientations is due to the difference in the orientation of boundary plane. These results are a direct experimental evidence for the utility and the validity of Σ for characterization of grain boundaries,

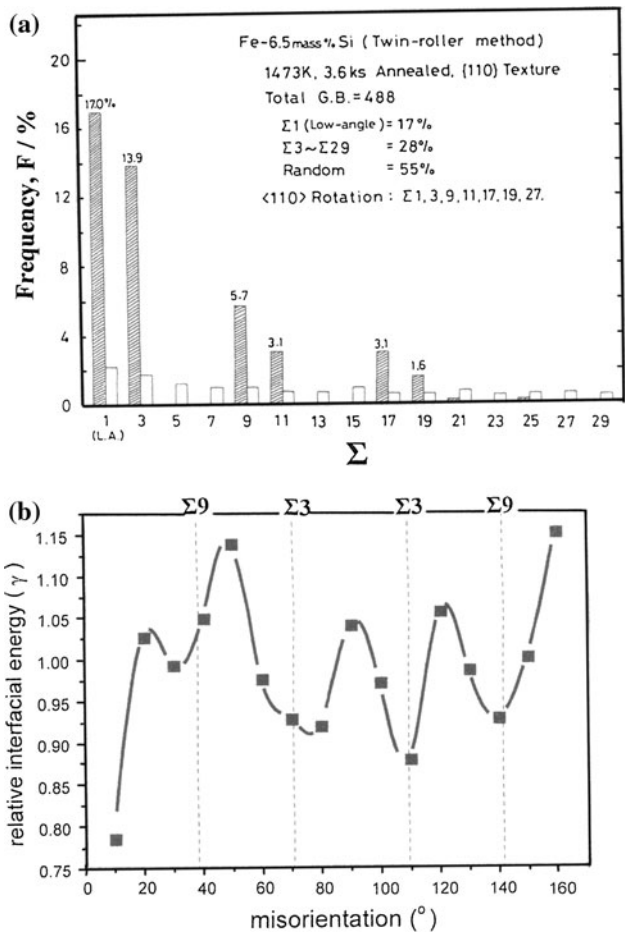

Fig. 5 **a** *Upper figure*: Frequency of occurrence of low-Σ (Σ < 29) for ⟨110⟩ textured Fe–6.5mass%Si alloy ribbons produced by rapid solidification from the melt and subsequent annealing; determined by Watanabe, Fujii, Oikawa, Arai: 1989 [45]. **b** *Lower figure*: Misorientation dependence of relative grain boundary energy γ_{gb} for the same ⟨110⟩ textured Fe–6.5mass%Si alloy ribbons; determined by Zimbouski, Kim, Rohrer, Rollet, Watanabe: 2003: referred to [48]

particularly for BCC boundaries without any specific difference in the area density of coincidence sites, as in the case of FCC boundaries with three groups of Σ values predicted by Smith [46]. On the other hand, there is another experimental study which supports the three different Σ dependences of boundary structure and energy in FCC crystals. Yamaura et al. [49] have studied structure-dependent intergranular oxidation in Ni–Fe alloy with FCC crystal structure. They found that coincidence boundaries show different levels of the oxidation activity amongst the three groups with specific Σ values as predicted by Smith. On the basis of these findings, the author would like to emphasize that the long pending dispute will disappear if the difference of Σ dependence of structural order predicted by Smith is fully recognized for FCC boundaries particularly with low-stacking fault energy. To my knowledge, such a consideration for Σ dependence of the grain boundary energy and other properties of coincidence boundaries has never been made except for the work done by Yamaura et al. [49]. Similar irregularity of Σ dependence of boundary properties might be observed for coincidence boundaries in intermetallics and ceramics where chemical composition of the grain boundary can drastically change depending on the boundary inclination [43, 50].

Importance of the effect of boundary inclination

The effect of the grain boundary inclination on grain boundary properties has been studied from different view points. For example, the effect of boundary inclination on the boundary energy began to be studied very early and still has been repeatedly investigated up to now using bicrystals [51–54]. In order to get some insight into the importance of the effect of boundary inclination, let us refer to an interesting result on the effects of boundary misorientation and inclination on intergranular corrosion of ⟨100⟩ and ⟨110⟩ tilt bicrystals of stainless steel in H_2SO_4 2 N solution, reported by Froment [55].

As shown in Fig. 6, for the case of intergranular corrosion at the ⟨100⟩ tilt boundaries, the extent of corrosion (L) depends on both the boundary misorientation θ and the inclination φ. It is also evident that the characteristic feature of the misorientation dependence of intergranular corrosion appears quite different depending on the boundary inclination because for some grain boundaries with specific misorientations, it depends more strongly on the inclination than the other boundaries. It is very likely that the origin of boundary inclination effect is due to the anisotropy of grain boundary phenomenon, particularly for tilt boundaries with respect to the orientation of a specific rotation axis, as well known in the case of intergranular diffusion. It is also worth mentioning that Otsuki [52, 53]

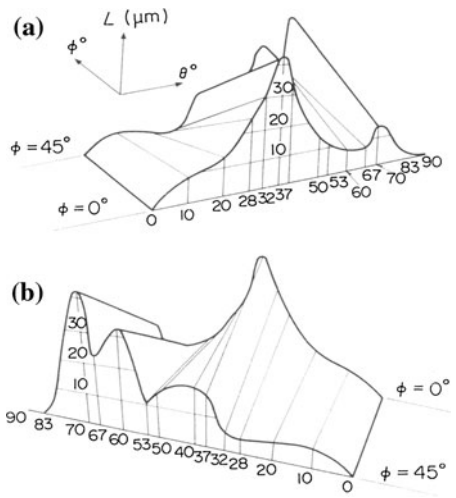

Fig. 6 Dependence of intergranular corrosion on grain boundary misorientation (θ) and inclination (φ) for $\langle 100 \rangle$ tilt stainless steel bicrystals in 2 N H_2SO_4 solution, determined by Froment [55]. Measurement of corrosion depth was made in the direction parallel to the tilt axis. *Note*: characteristic feature of misorientation dependence of corrosion depth drastically change with boundary inclination from the symmetric boundary inclination ($\varphi = 0$) to asymmetric inclination ($\varphi \neq 0$)

has developed a unique experimental technique for studying the boundary inclination effect by growing co-cylindrical bicrystal samples. This technique seems very powerful because of its capability to study the inclination effect over the whole range of inclination angle for tilt boundaries with a specific rotation axis. As seen from the literature, symmetric tilt boundaries with specific rotation axes (boundary inclination $\varphi = 0$) have been often used to study structure-dependent boundary properties as a function of the misorientation angle. This tacitly means that the effect of boundary inclination is fixed. On the other hand, in the case of asymmetric tilt boundaries ($\varphi \neq 0$), we need to quantitatively determine how much the boundary inclination can affect a given boundary property and whether the effect is significant or negligible, depending on the deviation from the symmetric boundary position. Grain boundaries in polycrystalline materials are not always of symmetric tilt type rather they are mostly mixed in character with a twist component. To the author's knowledge, the available quantitative data reported on the combined effects of boundary misorientation and inclination upon boundary properties is very limited. Further research is required to collect quantitative information and reliable data on structure-dependent boundary properties for future grain boundary engineering.

More recently, the distribution of grain boundary inclinations in polycrystalline materials has been studied by Rohrer et al. for metallic as well as ceramic materials [56, 57]. The distribution of boundary inclination is a new topological and statistical parameter which may affect boundary-related bulk properties of polycrystalline material, together with the grain boundary character distribution (GBCD). It should be mentioned here that it is difficult to uniquely determine the inclination of individual grain boundaries in a real polycrystalline material because grain boundaries are not always planar. They are mostly curved, except for the case of extremely large-grained 2D polycrystals. Accordingly, it is not easy to quantitatively describe the boundary inclination distribution with some divergence of orientation. However, such a challenging effort made by Rohrer et al. will bring about some useful solution. Thus, it is very important to establish experimental and theoretical basis of a possible approach to quantitative description of the inclination distributions of curved boundaries with various extents of curvature depending on grain size, boundary connectivity or the character of triple junctions. Further, we need to find some correlation between the inclination distribution and boundary-related bulk properties, for the future grain boundary engineering, in addition to that achieved so far by using GBCD.

GB microstructure bridging individual boundaries to bulk properties

It is well known that the presence of even a single boundary can drastically affect mechanical properties. The important examples are the plastic deformation and fracture of bicrystals of metals [58] and ceramics (Al_2O_3) [59]. As already mentioned in the preceding section, the activity of grain boundary strongly depends on the boundary structure and character, and also on geometrical arrangement of the boundary in the specimen. Another question is that how much the influence of grain boundaries can change with increasing the number or density of grain boundaries in thin wires (1D), thin films or ribbons (2D) and ordinary bulk (3D) polycrystalline samples. Here, we should not forget that the character of existing grain boundaries is never the same, rather it normally shows a large variety in polycrystalline materials produced by conventional processing methods.

Now let us focus our discussion on the microstructure associated with grain boundaries, termed "grain boundary microstructure". Strictly speaking, the microstructure in a polycrystal is very heterogeneous, in terms of the boundary character/structure and geometrical configuration. For quantitative description and discussion on the effects of grain boundaries on bulk properties in polycrystals, we need to introduce several new microstructural factors which can lead to a quantitative and precise description of the grain boundary microstructure. The author has introduced the following statistical factors in the early 1980s [24]: the grain boundary character distribution (GBCD),

the grain boundary connectivity, the grain boundary inclination distribution, and some other factors too. Here, we look at some examples to confirm how effectively the first two microstructural factors (GBCD) and the boundary connectivity can work in our understanding and controlling grain boundary-related bulk properties in real polycrystalline engineering materials.

As a first step, we need to quantitatively characterize the grain boundary microstructure in polycrystalline materials with grain size ranging from ordinary micrometer to nanometer. This procedure is not difficult anymore nowadays after the advent of SEM-EBSD/OIM developed by Adams et al. [20, 21]. An example of analysis of grain boundary microstructure by FEG-SEM/OIM is shown in Fig. 7 which illustrates FEG-SEM/OIM micrographs for ultra-fine grained sample of sintered βSiC with the average grain size of 1.1 μm [60]. We can easily obtain the necessary information about the grain boundary microstructure defined by the grain boundary character distribution (GBCD), the grain boundary connectivity associated with GBCD, and the grain size distribution from OIM by using the standard software, as long as the image quality of EBSD pattern is suitable for analysis. The advent of SEM-EBSD/OIM brought about a new stage of quantitative/statistical analyses of grain boundary microstructures, grain boundary-related phenomena, and bulk properties in polycrystalline materials. For the design and control of grain boundary, i.e., Grain Boundary Engineering the basic features of the grain boundary microstructure in polycrystalline metallic materials have been discussed in depth by the author in view of the following issues [61–63]: (i) the relation between grain boundary character distribution (GBCD) and grain size, (ii) the relation between GBCD and texture, (iii) the relation between GBCD and chemical composition of material, and the (iv) relation between GBCD and crystal structure (e.g., bcc, fcc, hcp).

Grain size physically means the spacing between grain boundaries and is related to the density of grain boundaries. It has always been used as a key parameter controlling grain boundary-related bulk properties like "Hall–Petch relationship" to describe the grain size dependence of the flow and fracture stresses in polycrystalline materials [64, 65]. Since then, the grain size has been a key parameter in understanding bulk properties of polycrystalline materials [66, 67]. However, as stated in the previous section on bicrystal studies, the observed grain boundary phenomena are strongly dependent on the grain boundary structure and character. It should be pointed out that the grain size is only a geometrical parameter describing the area or volume density of grain boundaries in a polycrystal, and that does not have any physical relation to the grain boundary character and structure. Therefore, we need to find the relation between grain size and grain boundary character distribution (GBCD), in order to fully understand the grain size dependence of structure-dependent boundary-related bulk properties in polycrystalline materials. This is particularly important for nanocrystalline materials where the density of boundaries is extremely high.

Figure 8 shows the relationship between the fraction of special boundaries (low-Σ coincidence boundaries including Σ1 that is low-angle boundary) and the grain size for bulk polycrystalline samples of metals and alloys produced by ordinary thermo-mechanical processing [68]. Except for the case of Fe–6.5mass%Si polycrystalline ribbons produced by rapid-solidification and subsequent annealing [45], there is a general trend that the frequency of special boundaries goes down from almost 100% to about 15% with increasing grain size from a few micrometer to 1 mm,

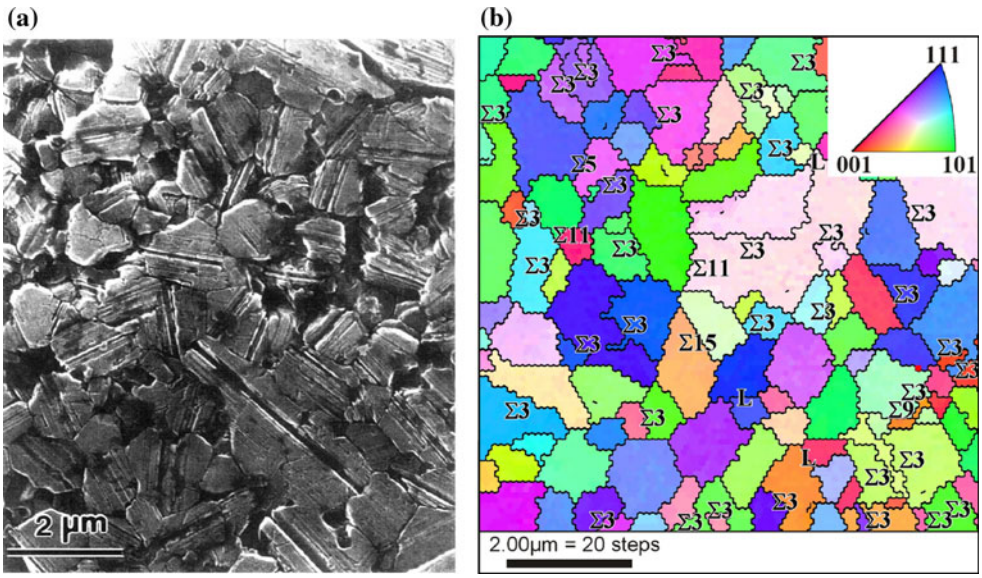

Fig. 7 An example of SEM-EBSD/OIM analysis of the grain boundary microstructure in a polycrystalline sample (fine-grained SiC) with the mean grain size of 1.1 μm [60]. The character of individual boundaries can be known from the Greek letter and a numeral for coincidence boundaries. Those boundaries without letter are high-angle random boundaries

although there is a large scatter amongst the studied materials which underwent more or less different processing conditions. It should be noted that the slope of the observed curve is almost equal to 2 (actually 2.3) which is generally recognized as the slope of the Hall–Petch relation. On the other hand, in the case of the Fe–6.5mass%Si ribbons with the initial grain size of 10 μm, the frequency of special boundaries goes up with increasing the average grain size after annealing of the as-solidified ribbon. This finding clearly shows that the relationship between the frequency of special boundaries and grain size can be quite different. Sometimes it can be just reversed depending on the processing method. On the basis of the results shown in Fig. 8, we can easily understand the reason why the ductility of polycrystalline materials generally becomes lower with increasing grain size. This is because the frequency of special low-energy boundaries, which are resistant to fracture, decreases with increasing grain size. In other words, the frequency of high-angle random/weak boundaries increases, in ordinary thermo-mechanically processed polycrystalline materials. It is very interesting to study how GBCD can change, depending on the material, the processing method and the processing parameters. This kind of basic knowledge is warranted in future studies. Surprisingly, the importance of the relationship between grain size and GBCD has not been recognized. The effect of grain boundaries on bulk properties have been primarily discussed from the view point of grain size alone, i.e., the density of grain boundaries. In 1980s Grabski et al. [69, 70] and the present author [24, 71, 72] pointed out the importance of the relationship of grain size with GBCD based on their experimental data. For example, recent arguments on the negative slope of the grain size

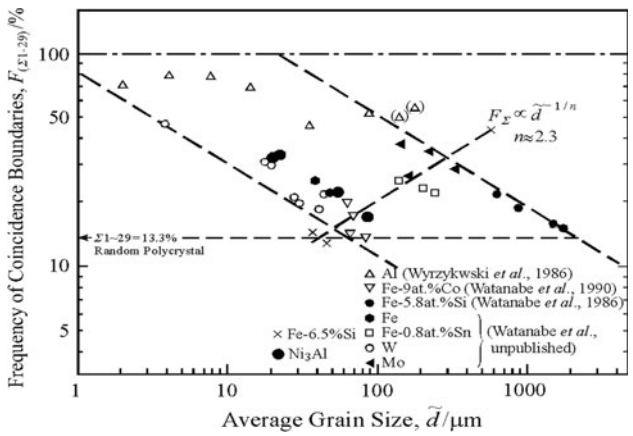

Fig. 8 Experimental data on the frequency of occurrence of low-Σ (<29) coincidence boundaries (including low-angle Σ1) as a function of the mean grain size in metallic bulk polycrystalline materials produced by thermomechanical processing, except Fe–6.5mss%Si ribbon samples produced by rapid solidification and subsequent annealing [68]

dependence of flow and fracture stresses in nanocrystalline materials also known as "Inverse Hall–Petch Effect" should be reanalyzed in connection with the above mentioned relationship. The present author has, however, discussed the relationship of GBCD with grain size, texture (the type and sharpness), composition/purity, and processing, in some detail [72].

In situ observation of grain boundary-related phenomena can provide the crucial role of grain boundaries in controlling such phenomena and hence, the bulk properties in polycrystalline materials. Early work on in situ observations on grain boundary character/structure-dependent fracture processes in polycrystals using SEM tensile stage revealed that the crack is formed at the random boundary that is aligned perpendicular to the tensile stress axis, and then propagate to connect other random boundaries resulting in a dominant intergranular fracture in typical brittle fracture mode [24]. On the other hand, when a mixed intergranular and transgranular fracture occurred (as indicated by the path A), a ductile fracture was observed depending on the type of grain boundary in front of a propagating crack. The characteristic features of fracture processes obtained from the in situ SEM-observation are schematically given in Fig. 9 [24]. The in situ observations of fracture processes in polycrystals have enabled to model, for the first time, a mechanism of GBCD-dependent fracture processes and to predict the fracture toughness as a function of GBCD and grain boundary geometry, later predicted on the basis of percolation approach to fracture process in 2D [73] and 3D [74] polycrystalline materials. The application of the percolation theory to GBCD-dependent percolation of the electrical current has been made by Nichols and Clarke [75]. Recent development of experimental techniques for quantitative and topological analyses of grain boundaries microstructures, particularly

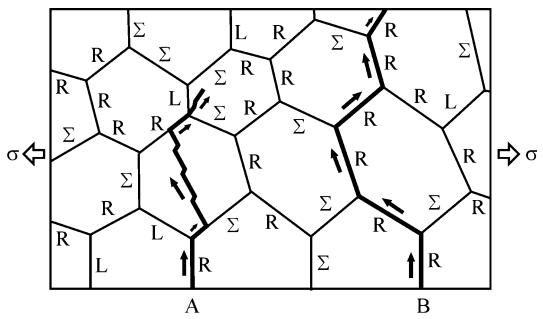

Fig. 9 Schematic representation of structure-dependent intergranular fracture processes in a polycrystal [24]. When an initially formed intergranular crack cannot continue to propagate because of meeting different types of grain boundaries, fracture proceeds by mixture of intergranular and transgranular fracture (Path A). On the other hand, when intergranular crack can propagate at connecting random/weak boundaries, typical intergranular fracture occurs showing severe brittleness

by OIM, has facilitated in obtaining optimum grain boundary microstructures for the generation of desirable properties and high performance in polycrystalline materials [62, 76–79]. The observed threshold value of GBCD (the fraction of special boundaries) for a drastic change of GBCD-controlled bulk properties [80–82] well corresponds to the prediction by the simulation based on the percolation approach to the transition from brittle to ductile fracture [74, 83–85]. Recent situation and progress in the field of grain boundary engineering are detailed in special issues of several journals on GBE [86, 87].

A new development from interface science to interface engineering

It is very challenging to find a way how to use our current knowledge of Interface Science developed during the past half century, in order to solve many pending issues pertaining to polycrystalline materials. One of the serious pending problems is the control of the brittleness of engineering materials. There is a general tendency that when the strength of materials is increased, they inevitably become more brittle and their ductility tends to go down. This is a long pending dilemma troubling materials scientists and engineers. We are asked the following question: is it possible to produce a polycrystalline material with much higher strength and high fracture toughness than conventional materials by controlling the grain boundary microstructure in the same material? Historically serious accidents which were caused by fracture of large scale structures, such as ship, aircraft, and nuclear power station and on a smaller scale, the fracture of machine components have been found to be often due to severe intergranular fracture which occurs suddenly during service. To solve this pending problem is an urgent requirement; however, there has been no established way to solve such a problem. This is probably because the basic knowledge of "Interface Science" was not sufficient to lead to the development of a new discipline of "Grain boundary and Interface Engineering" which could be used for controlling intergranular brittleness in structural materials. We need to establish a new discipline involving the designing and manipulating optimum grain boundary and interface microstructure, in order to produce desirable bulk properties and high performance, and even to create a new function.

Let us look at early achievements of grain boundary engineering (GBE) which enabled the control of intergranular brittleness in so called "intrinsically brittle" polycrystalline metallic materials". Severe brittleness of refractory metals, intermetallics, and ceramics are well known. Iron–silicon alloys with high silicon content beyond 3mass% have been widely used because of their excellent soft magnetic properties. A classical example is Fe–6.5mass% Si alloy which has almost zero magnetostriction. More recently, the severe brittleness of polycrystalline Fe–6.5mass%Si alloy has been successfully controlled and high performance ductile Fe–6.5mass%Si alloy ribbons with ⟨100⟩ and ⟨110⟩ sharp texture have been developed. This is done by the introduction of a high fraction (more than 45%) of low-energy boundaries resistant to intergranular fracture, through rapid-solidification and subsequent annealing that are following the concept of grain boundary engineering [45]. Probably, this is the first experimental evidence for the utility of the concept of grain boundary engineering to solve long pending materials problems performed at the end of 1980s. Since then, grain boundary engineering has been actively attempted by several research groups and successfully applied to the control of intergranular brittleness due to intergranular fracture and corrosion in metallic, intermetallic, and ceramic materials. A few notable examples are nickel-based alloys [88, 89], molybdenum [62, 90], Ni_3Al [91, 92], oxide ceramic Al_2O_3 [59], and non-oxide ceramic SiC [93]. These early achievements of grain boundary engineering (GBE) during 1980–1990 have provided reliable evidence for the utility of GBE over 1980s–1990s.

Another direct experimental evidence for the utility of the grain boundary engineering is to control intergranular brittleness in "intrinsically brittle materials" such as polycrystalline Ni_3Al, by controlling grain boundary microstructure. Figure 10 shows the result of tensile tests for polycrystalline Ni_3Al (ordered LI2 alloy) without boron [92]. It is well known that without boron addition, it is very brittle at room temperature due to high propensity to intergranular fracture. However, it is evident that the brittleness can be drastically improved by reducing the fraction of high-angle random/weak boundaries (R) or reversely, by increasing the fraction of low-angle and low-Σ coincidence boundaries (low-energy/fracture-resistant boundaries). This has been achieved by floating-zone directional solidification/subsequent annealing, first attempted by Hirano [91]. Surprisingly, "intrinsically brittle" polycrystalline Ni_3Al without boron was found to possess a high ductility, more than 50% elongation at room temperature. However, once the fraction of high-angle random/weak boundaries is raised by cold rolling and subsequent annealing, the observed ductility disappears and does not come back again as long as the fraction of random boundaries remains at almost the same level. This clearly indicates that even severe intergranular brittleness of "intrinsic brittle" polycrystalline Ni_3Al without boron can be controlled by reducing the fraction of high-angle random/weak boundaries. Quite recently, Hirano et al. have developed ductile thin films of polycrystalline B-free Ni_3Al for use as high temperature material [94]. It should be mentioned here that the addition of B was once thought to be effective for

controlling intergranular brittleness of polycrystalline Ni_3Al [95], but later it was found that addition of boron causes abnormal grain growth resulting in the occurrence of severe intergranular brittleness during service at high temperature [96]. The necessity of re-examination of conventional approach to intergranular brittleness in Ni_3Al in view of moisture-induced hydrogen embrittlement has also been pointed out [97].

In the author's opinion, it has been almost established that the long pending problem of intergranular brittleness in metallic and ceramic polycrystalline materials can be controlled by manipulating the grain boundary microstructure: particularly GBCD and the grain boundary connectivity. There are numerous experimental evidence for the control of different intergranular brittleness, arising due to intergranular-corrosion, stress-corrosion cracking in nickel-based alloys [88, 89], stainless steels [80, 81, 98–100], and ferritic–martensitic steel [101]. In addition, the concept of GBE has been successfully employed to address the issue of intrinsic intergranular brittleness of Al–Li alloys [102] and molybdenum [62, 90] and also for enhancement in tensile strength in copper [103], creep strength in nickel and Ni-based alloy [88, 104–106]. GBE is also effective in tackling the issue of fatigue fracture strength [107, 108], intergranular oxidation resistance [49, 109], and for the control of segregation-induced embrittlement in nanocrystalline nickel [110] and hydrogen embrittlement in Ni-based alloy [111]. Recent special issues on GBE [86, 87, 112, 113] and review papers written by those researchers who have been deeply involved in GBE [61–63, 76–79, 114, 115] may help the reader to understand and know state-of-the art of the discipline of Grain Boundary and Interface Engineering. A summary of the above discussion as presented in Table 2 provides an idea of the previous applications of GBE to various materials and pending problems.

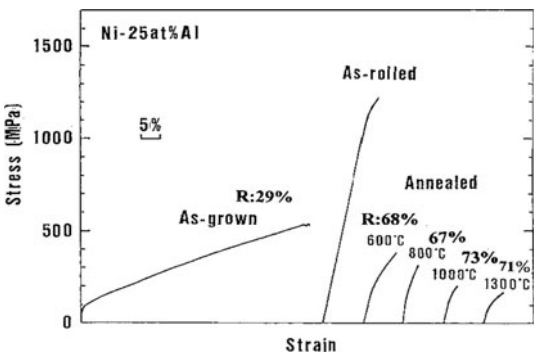

Fig. 10 Experimental evidence for GBCD-controlled deformation and fracture in polycrystalline samples of Ni_3Al without boron, produced by different processing (as unidirectionally solidified, as-rolled, rolled and annealed at different temperatures [92]

Finally, let us examine the applicability of GBE to advanced functional materials such as photovoltaic polysilicon. Unfortunately, there is not much literature except the most recent article by the present author and co-worker [116]. A quantitative study of structure-dependent electrical activity of grain boundaries in silicon is reported in [117, 118]. As shown in Fig. 11, the electrical resistivity, which is a key factor controlling the efficiency of conversion of solar energy to electricity, strongly depends on the details of the grain boundary microstructure, i.e., GBCD and geometrical arrangements of different types of grain boundaries, as expected by the prediction based on percolation process of electrical current in polycrystals [75]. When the fraction of high-energy random boundaries is controlled to a value lower than 20%, one can expect a much lower resistivity without recombination of electron and positive holes at random boundaries, irrespective of geometrical configuration of boundaries in polysilicon samples produced by special unidirectional/rotational solidification processing method.

A new challenge to grain boundary and interface engineering

In the twenty-first century, there are still a number of pending problems which need to be solved using the concepts of grain boundary engineering. In addition, there is a possibility to impart such functionality to materials that is absent in the original condition by the application of grain boundary and interface engineering, as briefly introduced below. We have already learnt that grain boundary engineering can effectively work in controlling such grain boundary phenomena which primarily limit the performance and lead to the degradation of the bulk structural and functional properties of polycrystalline materials. In principle, the problems pertaining to different types of brittleness/embrittlement caused by intergranular corrosion, segregation, oxidation, and fracture have been almost solved. New patents for technological applications of GBE to the production of new materials have been successfully and increasingly obtained. One of the first few examples is the one demonstrated by Palumbo of Integran Technologies Inc. in Canada.

Let us consider the new challenges in the future activities pertaining to grain boundary and interface engineering for new structural and functional materials with more desirable properties and higher performance than currently existing materials. We simply consider our target based on the following two points: (i) what kind of material function and property (among mechanical, physical, chemical, elctromagnetic, optical, biological properties, and any other) are likely to be required for future engineering applications, and

Table 2 Recent achievements of grain boundary and interface engineering

Material	Improved property	Boundary phenomena	Processing method	Ref.
Fe–6.5%Si	Soft magnetic Prop. brittleness	Magnetization fracture	Rapid-solid./annealing	[45]
Ni-alloy	Stress-Corrosion	Corrosion	Thermomechanical	[166]
Ni_3Al	High-temp. strength	Fracture	Floating-zone-solidif.	[92]
Nano-Ni	Electrical/Magnetic/Mech.	GB. scattering	Pulse-electrodeposition	[167]
Alloy600	Corrosion-resistance	Corrosion	Thermomechanical	[89, 168]
Ni	Creep-strength	GB. Sliding	Thermomechanical	[104]
Al_2O_3	Creep-strength	Segregation/Diffusion	Y Doping	[169]
Al_2O_3	Creep-strength	Segregation	Y Doping	[170]
Al_2O_3	Creep-strength	Segregation/Sliding	Zr Doping	[171]
Pb-alloy	Acid-battery-corrosion	Corrosion	Deep-cycling	[172]
Fe–Pd Alloy	Shape-memory	Domain interaction	Rapid-solid/annealing	[173]
Mo	Brittleness	Segregation/Fracture	Thermomechanical	[62]
Ni–Cr alloy Creep	Stress-corrosion	Sliding, Corrosion	Thermomechanical	[174]
α-brass	Tensile ductility	Fracture	Iterative Processing	[175]
304 steel	Corrosion-resistance	Corrosion	Thermomechanical	[98]
Al–Li alloy	Superplasticity	Sliding	Thermomechanical	[102]
Fe–Ni alloy	Oxidation-brittleness	Oxidation/Fracture	Rapid-Solid./annealing	[176]
Fe–Sn alloy	Brittleness	Segregation/Fracture	Magnetic annealing	[139]
Al, Al–Mg	Superplasticity	Sliding	ECAP-annealing	[177]
Two-phase-steel	Superplasticity	Sliding	Thermomechanical	[178]
304 Steel	Weld-decay	Corrosion	Prestrain annealing	[179]
Fe–Co alloy	Damage Rejuvenation	Cavitation/Sintering	Magnetic annealing	[180]
Ni-alloy	High-cycle fatigue	Fracture	Thermomechanical	[181]
316 Steel	Corrosion-resistance	Corrosion	Prestrain annealing	[81]
Fe–Si–B	Soft-Magnetic	Crystallization	Magnetic crystallization	[182]
304L	Corrosion-resistance	Corrosion	Thermomechanical	[80]
304 Steel	Weld-decay	Segregation/Corrosion	Prestrain annealing	[99]
Poly-Si	Photovoltaic	Solidification	Uni-dir./Rotation.Solidf.	[116]
Al	Fatigue Strength	Fracture	Thermomechanical	[108]
SUS304	Corrosion-resistance	Solidification	Laser surface melting	[183]
Sn Solder	Thermal fatigue	Sliding/Fracture	Thermal cycling	[184]
Nano-Ni	Ductility	Segregation/Fracture	Deposition/Annealing	[110]

This table lists up the articles which have reported on GBE with experimental evidence for improved properties and performance or generation of a new function

(ii) how to control the grain boundary microstructure and interfaces more effectively to confer a desirable function and reliable performance to a given material, exactly as expected. In a sense, we might be able to transform an existing material into a new material with new function and/or property. For this purpose, we need to develop a new processing method, as our pioneering researchers and engineers have envisioned. The author would like to introduce several new challenges which are going on in the research area of grain boundary and interface engineering during the past 10 years.

Quite recently, the development of new types of processing methods under magnetic and electrical fields has been drawing increasing interest of researchers who are involved in texture and microstructure control through recrystallization, solidification, and transformation. In fact, we can find the root of this kind of study on the effect of a magnetic field on metallurgical processes for the purpose of development of high performance magnetic materials in the early last century [119]. However, this has not been seriously taken into microstructural control, except for magnetic materials [120, 121] and martensitic transformation [122, 123] until recently. Nevertheless, after the development of a helium-free superconducting magnet in the 1990s, high magnetic field became available even at a university laboratory. This has greatly enhanced interest of

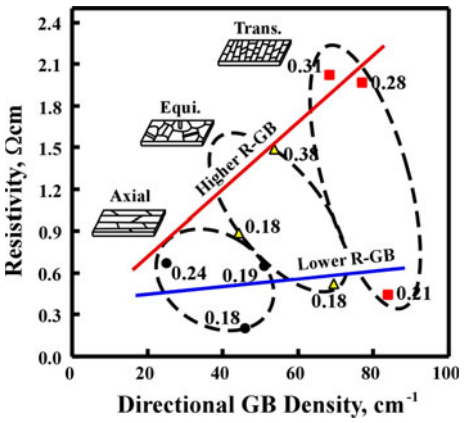

Fig. 11 The effect of grain boundary microstructure on the electrical resistivity in polysilicon samples produced by unidirectional/rotational solidification [116]. The numbers indicate the fraction of random boundaries which play as more effective scattering center among different types of boundaries. Note that the electrical resistivity tends to be less sensitive to the directional configuration of random boundaries when the fraction of random boundaries is lower

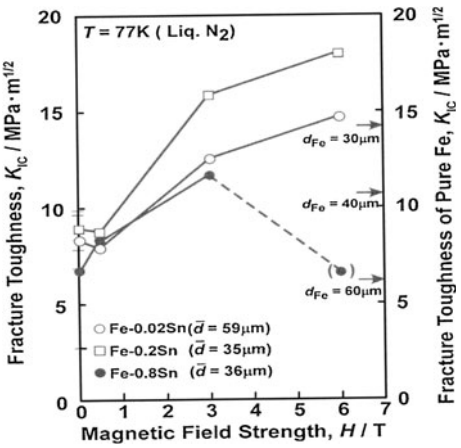

Fig. 12 Fracture toughness measured at 77 K for Fe–Sn alloys annealed at 973 K for 6 h with a magnetic field of different strength. For comparison, the fracture toughness of pure iron with different grain sizes is indicated by the *arrows* along the vertical axis of right hand side. *Note*: Fracture toughness of Fe–Sn alloys increases with increasing applied magnetic field during annealing. After Tsurekawa et al. [139]

researchers and driven them toward a new direction with regard to the application of a high magnetic field for inventing a new processing technology. Such a technology involves microstructure and texture control based on: magnetic annealing [124–128], aging [129], solidification [130, 131], sintering [132], and phase transformation [133–138] in metallic materials. Furthermore, new technologies for controlling segregation-induced intergranular embrittlement in iron [139] and for rejuvenation of damaged metallic materials such as iron alloys [140] have been developed by the author's group.

A brief introduction of our recent achievement toward the control of segregation-induced intergranular brittleness is given below for the iron–tin system. Tin (Sn) is well known as detrimental element causing severe intergranular brittleness due to grain boundary segregation in iron and steels as a result of its extremely low solid solubility and high grain boundary enrichment ratio [141]. Nevertheless, tin-galvanic coated corrosion resistant steel sheets are widely used in our daily life so that a serious material problem has been raised after repeated recycling of used steel scrap. The concentration of detrimental elements like Sn and copper (Cu) in steels has kept constantly increasing statistically and their performance and properties such as ductility and corrosion resistance tend to go down. Accordingly, it is urgent to solve this problem. Quite recently we have found the possibility that segregation-induced intergranular brittleness in the Fe–Sn alloy system can be controlled by high magnetic field annealing [139].

Figure 12 shows the fracture toughness as a function of magnetic field strength for magnetically annealed specimens[1] of iron–tin alloys with different tin concentrations ranging from 0.02 to 0.8 at%. It is evident that the fracture toughness of iron–tin alloys increases with increasing magnetic field strength, irrespective of tin concentration. Surprisingly, the values of fracture toughness became higher for magnetically annealed specimens than pure iron in the range of applied magnetic field strength beyond 3 T. For comparison, the fracture toughness of pure iron with different grain sizes is indicated by the arrows along the vertical axis of right hand side of the figure. The reason for a much lower level of the fracture toughness for the Fe–0.8at%Sn alloy specimen, which is magnetically annealed at 6 T, is probably due to the formation of second-phase at grain boundaries. The origin of observed magnetic field effect is explained on the basis of the magnetic free energy in ferromagnetic Fe–Sn alloy which is one order of magnitude lower than the grain boundary segregation energy so that "atom cluster" of tin with extremely small susceptibility (2.7×10^{-8}) must be ejected from even high-energy random grain boundary. Thus, the grain boundary engineering by magnetic field application has been proved to be able to solve long pending segregation-induced intergranular brittleness, at least for the iron–tin alloy system.

[1] The 85% rolled sheet specimens were prepared by ordinary or magnetic annealing at 973 K ($T/T_c = 0.95$, T_c: the Curie temperature) for 6 h. The average grain size of annealed specimens was almost similar for the three alloys, namely the density of grain boundaries was kept at almost similar level, although there was some difference less than twice for Fe–0.02at%Sn alloy. The frequency of random boundaries which can be preferential sites for segregation was almost 80% for the three alloys. The fracture toughness was measured by the three-point bending test. The details of the experimental procedure are presented in the original paper [139].

Recent reviews on the magnetic field application for microstructure, texture, and bulk properties may be useful for the reader to know some physical basis of the effects associated with a magnetic field and resultant bulk properties of polycrystalline materials produced by the application of magnetic field [7, 142–144].

Here, a brief introduction of recent studies on the application of an electric field is useful. Conrad and coworkers have recently studied the effects of an electric field and current on phase transformation for controlling microstructure in metals and ceramics [8], and also for enhancement in superplasticity through grain growth control in ceramics like Y-doped ZrO_2 [145]. On the other hand, Choi et al. have observed an interesting effect of electric field on grain boundary migration in alumina Al_2O_3 [146]. They found that grain boundary migration rate depends on the applied bias direction and chemical composition which affect electrostatic state potential of grain boundaries due to doping. Their finding suggests that the application of an electric field can be more effectively utilized in order to control the microstructure through grain boundary migration and grain growth in ceramics than metallic materials. Unfortunately, to the author's knowledge there is no available literature on this topic.

Finally, the author would like to introduce two new concepts which have been recently proposed and will be branches of "the grain boundary engineering" in future. One is "Grain boundary junction engineering" proposed by Gottstein and Shvindlerman [147] and the other is "Grain boundary complexion" by Dillon, Harmer and coworkers [148, 149]. We begin with the concept of grain boundary junction engineering. Microstructural evolution in polycrystalline materials always involves grain growth associated with grain boundary migration. We have already discussed that the migration of individual grain boundaries strongly depends on the boundary character and structure [42]. However, it is important to note that individual grain boundaries cannot move independently but have to move interactively among 2D or 3D network of grain boundaries in a polycrystal. Accordingly, the interacting points of grain boundaries such as triple and quadruple junctions have to move to produce grain growth in polycrystals. Gottstein and Shvindlerman [147] have suggested that grain growth in polycrystals is controlled by the mobility of such boundary junctions under certain circumstances. This will provide us a clear view of the evolution of optimum grain boundary microstructure, from the view point of important roles of boundary junctions or the grain boundary connectivity, already stated in this article. There is already some experimental evidence for structure-dependent roles of triple junctions as preferential sites for grain boundary phenomena, such as intergranular corrosion [150], cavitation during superplastic deformation [102], and phase transformation [151]. More recently, the constraint of lattice strain associated with different types of triple-junctions has been investigated by microhardness testing for polycrystalline molybdenum [152, 153]. Triple junction hardening was found to be smaller at the junctions composed of low-angle and low-Σ boundaries than that at the junctions composed of random boundaries. This difference in the hardening depends on the grain boundary connectivity, becoming more significant with a decrease in carbon content in molybdenum. Thus, the important roles of triple junctions and grain boundary connectivity in the percolation process of crack propagation in polycrystals have been evidenced [153]. However, to the author's knowledge, structure-dependent roles and effectiveness of different types of boundary junctions have not yet been fully understood. To take the important role of boundary junctions into account could be a future work on this subject.

Quite recently Dillon, Harmer and coworkers have proposed a new concept of "Grain Boundary Complexion", as named by them [148], on the basis of HRTEM observations of grain boundaries associated with the normal and abnormal grain growth in ceramics. One such example is alumina with different dopants. The authors have identified six different types of GB complexions in similar view point of phase transition, and treated as analogous to phases designated as "complexions" [149]. This concept seems useful for more precise and quantitative study of grain boundary structures, particularly for ceramic grain boundaries with much more complicated structure due to addition of dopants than those of metallic materials. Future development and utility of this concept is very interesting from the view point of interface kinetics deeply involving materials processing. In fact, the effect of grain boundary structural transformation have been carefully investigated in metals, on grain boundary migration in aluminum bicrystals [154, 155] and sliding in zinc bicrystals [156]. It has been revealed that the temperature dependence of boundary migration and sliding abruptly changes at a certain critical temperature T_c depending on the type of grain boundary and material purity. The higher T_c was observed for low-angle boundary and low-Σ boundary, suggesting the higher thermal stability of these boundaries, than high-energy random boundaries. This kind of experimental study on the effect of grain boundary structural transformation may be indispensable to full understanding of microstructural evolution [42, 155] and mechanical properties [157] in polycrystalline materials at high temperatures.

Table 2 presents a summary of recent achievements of grain boundary engineering (GBE) applied to different types of polycrystalline engineering materials. It is evident that a number of tasks pertaining to GBE have been

performed and to result in development of several new methods for grain boundary engineering. A further new challenge would be made by active researchers to solve remaining pending materials problems or to impart new functionality in advanced materials.

Future prospect of low-dimension (1D, 2D) interface engineering

It is suggested that the effect of grain boundary and interface becomes more significant as the dimension and size of the specimen becomes smaller. This is evidently recognized in the case of micromachines or micro-electrical mechanical system (MEMS). Component materials are used in the shape of thin line and film contacting each other in MEMS. In a very tiny part, the presence of a single grain boundary or interface can generate a new function or totally degrade the operating function, depending on the nature of grain boundary/interface and its location in the part. This is similar to what is expected from the case of a bulk bicrystal sample which may be considered as magnified case of MEMS. As is well known, failure of electrical circuit is often caused by electromigration along the grain boundary or hillock formation at grain boundary triple junctions [158, 159]. However, to the author's knowledge, the prevention of failure of electrical circuit due to the presence of grain boundaries has not been fully solved yet, although a rapid and great progress in thin film studies and technology has been made in recent years [160]. Probably, this is due to the lack of basic knowledge about the nature and behavior of grain and interphase boundaries, and also highly sophisticated fabrication technique is yet to be developed. Moreover, there is a lack of basic knowledge about the effects of electrical field, electric current, and magnetic fields on grain boundary phenomena involving the electrical circuit and connects, which is closely related to the subject that we have discussed in the preceding section. Evidently, till date, we are still in the premature stage of Interface Engineering at the time of 2010.

The effect of grain boundary and interface may become more serious in thin line or thin film than ordinary bulk materials, I would like to point out the size effect of machine components in MEMS whose size at least 10^3–10^5 smaller than that of ordinary machines and large structures like air craft and space shuttle. From our previous experience on bicrystal fabrication and nanotechnology, it seems possible to artificially introduce desirable grain boundaries or interfaces in the local position more precisely as expected by using modern processing techniques. Quite recently Gleiter has presented his opinion regarding the future direction of Materials Science and Engineering, particularly Interface Science and Engineering [161–163]. His message is very instructive and useful for our thinking about future direction for those researchers who are presently involved in basic or applied studies of interfaces in materials. Now we need to obtain a new knowledge about atomic and electronic structure of organic/inorganic interfaces for future interface engineering of multifunctional materials [164].

The most recent work of Ikuhara and co-workers at the University of Tokyo on "Nanowire design by dislocation technology" is a good example of future prospect of Grain Boundary and Interface Engineering [165]. They have successfully fabricated nanowires containing low-angle grain boundaries in order to generate the electrical activity associated with grain boundaries in non-conducting

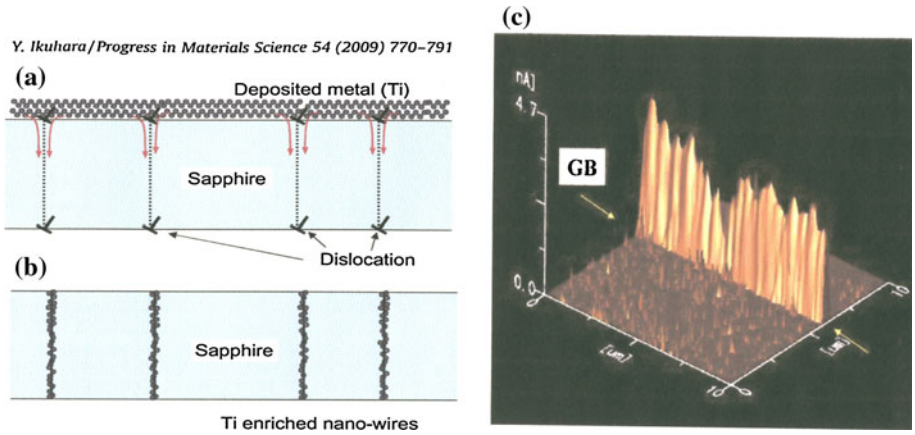

Fig. 13 Schematic diagram of a new Nanotechnology of "Dislocation Boundary Engineering" which can confer electrical conductivity to non-conductive ceramics like alumina Al_2O_3, by introduction of low-angle dislocation boundary, recently proposed and realized by Prof. Y. Ikuhara and coworkers [165]. **a**, **b** the principle of the dislocation engineering, based on the introduction of dislocations and low-angle boundary, and the decoration of dislocation lines by Ti-doping for generation of electrical conductivity. **c** Electron current mapping image for the [1100] 2° tilt boundary observed AFM-contact mode under the applied voltage of 100 V

ceramic alumina Al_2O_3. The basic concept of fabrication processes of one-dimensional nanowires is shown in Fig. 13a, b. After introduction of dislocations by plastic deformation of an alumina single crystal, the generated dislocations are decorated by Ti atoms to produce electrical conductivity in non-conductive alumina. In Fig. 13c, we clearly see what kind of characteristic feature of electrical activity can be generated locally at the position of individual dislocations composing a low-angle boundary. It is very exciting to imagine that such a new function can be synthesized as exactly designed according to 1D-Dislocation and 2D Interface Engineering.

It is well known that the density of dislocations composing a low-angle boundary can be controlled by controlling the boundary misorientation angle on the basis of the classic Read-Shockley theory of dislocation boundaries so that the local electrical activity of nanowire can be designed by controlling the spacing of grain boundaries and the misorientation angle of individual boundaries. It may be possible to synthesize the generated local electrical functions and activities associated with individual grain boundaries to produce a new synthesized function. Thus, the recent achievement by Ikuhara and co-workers is a good example and an evidence for that the legacy of learning from important works by pioneers can greatly help in research activities in the field of grain boundaries and interfaces. We should enjoy the versatility and potential of grain boundaries and interfaces. An active researcher always enjoys new challenges.

Summary

A brief introduction of the early phase of basic studies on grain boundary structure and properties has been given, to explain historical background of the concept of grain boundary engineering first proposed by the present author in the early 1980s. The importance of fundamental knowledge of structure-dependent grain boundary properties and a demand for development of a new processing method are emphasized to establish the growing area of the grain boundary and interface engineering. Recent capability of quantitative characterization and control of the grain boundary microstructure has enabled to confer desirable bulk properties and high performance to bulky polycrystalline materials in accordance with the strong demand for solving pending materials problems, for example, the control of intergranular brittleness in engineering material. Grain boundary engineering has been achieved not only for the structural materials but also for functional materials by applications of new processing methods. However, most of such studies are dedicated to mostly single phase metallic materials. Unfortunately interface engineering involving interphase interfaces is still premature. In the twenty-first century, the discipline of grain boundary and interface engineering has a lot of promise for low-dimensional (1D, 2D) components of micro-electrio mechanical systems (MEMS) with a newly synthesized function, as well as for ordinary 3D polycrystalline engineering materials.

Acknowledgements I would like to express my sincere thank to my mentors, Dr. Donald McLean and Prof. Karl T. Aust for constantly encouraging and guiding me to a new front in the research field of grain boundaries where I have been always enjoying a new encounter and a new challenge with unlimited interest. I express my sincere thanks to my ex-students and co-workers, particularly Prof. H. Kokawa and Prof. S. Tsurekawa who have shared the vision and new challenges of grain boundary engineering with me for many years. Collaboration with Prof. L. Zuo, Prof. X. Zhao, and Prof. C. Esling also helped greatly in the development of GBE by magnetic field application. My special gratitude goes to Prof. Yeng Cheng Huang (En-Sei Ko), my brother in-law, for his warmest encouragements for many years. Finally I would like to express my sincere thanks to Professor Satyam Suwas of Indian Institute of Science who kindly read and corrected the manuscript.

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