

Outstanding issues in electropulsing processing

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The processing of materials using electrical pulses utilises effects other than resistive heating to stimulate changes in their microstructure and hence the properties. The direct effect of electropulsing has not, however, been fully understood. There remain issues that delay the industrialisation of the method and there are gaps in the scientific understanding of mechanisms. The thermodynamic description of electropulsing is based on a few oversimplified geometric models. The corresponding kinetic description remains qualitative and less than helpful in stimulating applications. The role of electropulsing in multiphase materials where the magnetic permeability of the phases are different has not been explored. Experiments on electropulse-induced powder sintering reveal effects that are not related to resistive heating, but their origin has yet to be identified. Similar uncertainties apply to the mechanisms for electrically-induced crystal rotation and texture evolution. Electropulse-induced particle reconfiguration in liquid suspensions is a new field that is promising in helping clean melts from insulating oxides. These, and other aspects connected with applications and scaling are critically assessed.

Keywords: Electropulsing, Flash processing, Energy-saving manufacturing, Residual stress, Inclusions

Introduction

It would be adventurous to imagine that novel structures in the solid state can be induced in milliseconds, that materials exposed to service can be regenerated in similarly short times, and the molten metals can be purified by short duration treatments [1]. This and much more is promised in publications dealing with the treatment of materials using electrical pulses. However, it is now necessary to define and focus on difficulties if the field is to make substantive progress.

There is evidence that phase transitions and microstructural evolution may be steered into novel scenarios by an electrical field of a short duration [2]. Troiskii proved in pioneering work that plasticity can be a direct effect of electric current rather than due to side effects such as resistive heating [3, 4]. The latter has been discussed comprehensively by Okazaki et al. [5]. Furthermore, Ohmic heat can be kept to a minimum by using the short duration pulses when current density is high. Electroplasticity improves the workability of brittle metals such as tungsten, molybdenum and rhenium alloys [6]. The first of such engineering production lines was built in Kyongin Special Metal Co in 2005. In the last decade, considerable attention has been paid to the implementation of electroplasticity in the deformation of magnesium [7] and aluminium alloys [8]. The real challenge in this application appears in the deformation of multiphase and multicomponent alloys. The brittle intermetallic particles, for example that formed in magnesium alloys, have higher electrical resistivity than the matrix because they are rich in solute, consistent with Matthiessens rule [9]. The electric current density in the low conductivity particles is hence lower than that in the matrix [10]. The electroplasticity in this case can be less effective for the more brittle particles than that of the less brittle matrix. The situation is worse for smaller precipitates because of the higher solute compositions predicted by Gibbs-Thomson equation. Creative ideas to solve such problems are overdue because voids might form from the incompatible plastic deformation between the precipitate and electroplasticised matrix.

Electropulse-affected phase transitions reveal effects beyond electroplasticity. Misra implemented weak electric current in metal solidification and observed microstructural refinement in casts [11-13]. Barnak et al. reproduced the experiments in Sn-Pb alloys and found that the side effects and electromigration are not able to explain the experimental observations [14]. Although electroplasticity is thought to be based on electromigration [15], theoretical analysis reveals the force due to electromigration as at least 4 orders of magnitude smaller than that required to explain the observations [14, 16-17]. The enhanced diffusion accelerates the transformation from metastable to equilibrium states. However, the enhanced mobility is not necessarily to promote the nucleation rate [18]. Qin et al. calculated the extra free energy caused by the electric current and found that electropulse increased the equivalent undercooling in melt [19]. The extra undercooling contributes to the nucleation rate. The numerical results are consistent with the experiments by Barnak et al. [14, 20]. Such thermodynamic consideration of electropulsing has also been implemented to the design of micro-crack healing [21], phase separation [22] and nanostructured steel fabrication [23]. Electropulsing generates favourable microstructures in casting of large engineering components [24]. Scientific understanding of electropulsing processing, however, is limited. Theoretical considerations [10] are based on a few oversimplified geometric models and sometimes not suitable to describe the engineering materials. Experiments relate only to a few phenomena that leave many important topics unexplored. Some of these issues are highlighted here.

Problems in modelling of electropulsing processing

There is rich experimental evidence on the electropulsing-affected kinetics in microstructural transformations. Mizubayashi et al. found that electric current accelerated the structural relaxation of Cu-based amorphous alloys including $\text{Cu}_{50}\text{Ti}_{50}$, $(\text{Cu}_{30}\text{Zr}_{70})_{92.5}\text{Al}_{7.5}$ and $\text{Cu}_{50}\text{Zr}_{50}$ [16-17, 25]. Teng et al. reported that electropulsing enabled the crystallization of Fe-based amorphous alloys (e.g. $\text{Fe}_{73}\text{Si}_{9.5}\text{B}_{17.5}$, $\text{Fe}_{79}\text{Si}_7\text{B}_{14}$ and $\text{Fe}_{75}\text{Si}_{10}\text{B}_{15}$) to take place at a temperature which is 200 K lower more than its conventional crystallization temperatures

[26-27]. Riaz reported the current-induced crystallization of mould powder, where a glassy state would form in conventional solidification [28]. Those and other experiments demonstrate a common feature of electropulsing, that of accelerating transformation rate. However, a theory capable of predicting the quantitative effects has yet to be developed. Mizubayashi et al. analysed their experimental results using electromigration theory and found an apparent charge number of $Z=10^5$ is required [29-30]. It has $Z<4$ for a metallic atom. $Z=10^5$ corresponds to a cluster containing tens of thousands atoms. It is therefore speculated that electropulsing-stimulated a collective motion of at least 10^4 atoms. This speculation causes further questions: (1) how does the collective motion contribute to the transformation kinetics and (2) how does the friction from matrix to a cluster change when the cluster containing many more atoms? The electropulsing-accelerated microstructural transformation should at least be organized in either a database or phenomenological equation before more fundamental mechanisms are revealed, in order to enable the implementation of the knowledge to the processing of other materials.

Modelling of electropulse-assisted phase transition starts from the calculation of electric current associated free energy [31, 32]. This calculation requires the knowledge of electric current distribution in multiphase materials at various geometric configurations. For a metallic material with no net charge presenting in the space, the current distribution is obtainable by solving the Laplace equation [10]. This has been done analytically for a few cases, namely a spherical particle in a matrix [31], a cylindrical inclusion in a matrix [10], and an ellipsoid in an ellipsoidal matrix [32]. In all of those cases, the ratio between the characteristic length of embedded object and that of the matrix is assumed to be negligibly small. The theoretical results are hence suitable only for the prediction of nucleation of a new phase or defects in amorphous or eventually coarse-grained materials, and are not suitable for describing the systems containing boundary effects, e.g. the precipitates formation at grain boundary, nucleation to form nanostructured materials and microstructure transformation at surface. For the later mentioned cases, numerical calculation should be carried out to solve Laplace equation for obtaining the current distribution. This has rarely been reported. Indirect

experimental evidence on the effect of electropulsing on thermodynamics is available for many alloys. The formation of new phases using electropulsing is one such case [33]. The electropulse-affected precipitation in Al-4.5Cu [34], Mg-9Al-1Zn [7] and Al-3.3Mg [35] alloy is another case. The modification of the equilibrium phase diagram in the electropulsing processing should be considered, although no such work reported in literature. The information can be vitally important in design the electropulsing processing to the innovation of novel products. The difficult arises from the configuration dependent free energy due to electric current. For example, the chemical free energy of a phase is dependent on the chemical constitution, crystal structure and total amount of the phase only. However, the free energy due to electric current depends also on the configuration of the phase in the matrix, e.g. grain size, grain morphology and size distribution.

For multiphase alloys where the electrical conductivity and/or magnetic permeability of a phase is different from that of others [36], the skin effect is different from that of a pure metal. This has yet to be considered. There is also no calculation on the electric current free energy where the magnetic permeability of a phase is different from that of others.

Missing experiments in electropulsing processing

There are many experiments showing that electropulsing promotes the microstructural transformation; the electrical resistance of the material reduces in the process. Electropulsing-enhanced nucleation in solidification and recrystallization in cold work metals are within this consideration [14, 16, 20, 23]. The opposite cases where electropulsing retards the formation of low conductive phase, however, are not reported. The straightforward cases would include the observation of the electropulsing-retarded oxide formation in liquid metals, electropulsing-retarded porous formation in casting, electropulsing-improved anti corrosion and hydrogen resistance. The non-metallic oxides, gas bubbles, nitrides and hydrides are usually with high electrical resistivity than that of the metal matrix [37].

Another important parameter is the magnetic permeability. This parameter appears in the equation for calculating the electric current free energy. The value of the magnetic permeability and its spatial configuration contributes significantly to the free energy [31]. The change of the magnetic permeability value is significant around Curie temperature. However, the investigation and implementation of the electropulsing to the microstructural transformation of ferromagnetic alloys with permeability consideration is missing. For the observed electropulsing-induced microstructure transformation of ferrite, martensite and cementite phases in steels at lower than Curie temperature [23, 36, 38], there has been no intention to discuss the contribution from the magnetic permeability.

There is a demand to perform in-situ observation of both direct and side effects of electropulsing. Neutron diffraction may be able to determine the change of atomic and/or magnetic structure of a material under electropulsing. The skin effect, magnetic pinch and percolation current-induced heterogeneous heat rises should also be examined carefully. These fundamental studies would contribute to the understanding of electropulsing processing.

Electropulsing-induced residual stress removal and defects elimination has been reported in a number of cases [39, 40]. However, engineering application of this technology has not been seen. This is worth to explore.

Unclear effects of electropulsing

Electropulsing-induced texture formation occurs in the recrystallization of silicon steel and other alloys [41-42]. The mechanism is, however, not resolved. It is known that the ferromagnetic metals possess significant electrical resistivity anisotropy [43]. The formed crystals in electromigration have preferred crystal-orientation in order to maximize the system electrical conductivity [44]. Crystal rotation that allows the lowest electrical conductivity direction parallel to the electric current direction is able to reduce the system

free energy. The electropulsing in the cold worked silicon steel may stimulate such rotation. The preferred orientation of grains may be responsible for the observed texture. However, this has neither been discussed nor clarified in literature. Implementation of electromagnetic field to crystal orientation selection is an interesting topic [45].

It is reported that electropulsing causes sudden reduction of electrical resistance and change of atomic element distribution in a packed oxide powders [46]. The observed change of electrical resistance is proved not due to thermal effects but is rather dominated by field-induced dielectric breakdown. The current-induced element reconfiguration has not been fully understood.

Raj et al. found that the application of direct or alternating voltages to ionic ceramic powder during heating in a furnace led to ceramic body densification within a few seconds [47]. This has been demonstrated in many ceramic materials, such as nanograin zirconia [48], cubic yttria-stabilized zirconia [49], gadolinium-doped barium cerate [50] and many other materials. External temperature measurements have suggested that the ceramic temperature during flash sintering is not high enough to produce the observed mass transport in a period of time of a few seconds. Therefore, it was proposed that additional mechanisms beyond Ohmic heat may be responsible [51]. The mechanism, however, has not been identified. Zapata-Solvas et al. applied the technology to the sintering of some covalent ceramic powders. Their experiments indicated the major effect of Ohmic heat effect but other mechanism were unable to exclude [52].

Potentials in application of electropulsing to particle manipulation

Manipulation of the electrically neutral particles in liquid using external electromagnetic field has significant implementations in metallurgy, medication and chemical processing. Electropulsing has been found to exert a force to the particles from the centre of the liquid towards the surface [21]. The force is found dependent on the discrepancies between the

electrical properties between the particles and matrix. This has been applied to remove the non-metallic inclusions from liquid steel [36]. The force is different from the forces in magnetophoresis or electromagnetophoresis [53, 54]. It is possible to develop the technology to handle the particles/droplets in plasma and in other types of fluids [55]. The properties of the force have not been fully characterised. More comprehensive studies are needed to establish the technology for other suspensions.

Summary

- 1) The application of electropulsing in materials processing undoubtedly has potential. In comparison with conventional thermomechanical processing, it is rapid, consumes less energy, has a lower environmental impact and less capital investment. However, statements like these need justification beyond laboratory scale experiments.
- 2) There are mechanisms proposed for a variety of experimentally observed effects. However, there is no single case where the theory has been applied quantitatively. This limits confidence in the interpretations.
- 3) Speculation that the electrical current contributes to the free energy, and hence explains the changes in phase fractions or phase types, requires justification that in principle should be straightforward to establish. After all, it is routinely possible to account for the effects of stress, strain, magnetic fields and pressure on phase diagrams by supplementing any chemical free energy change.
- 4) It is possible that numerical rather than analytical methods need to be developed to explain complex effects observed in multiphase alloys, especially where the volume fractions of the different phases are similar with no minor phase present.
- 5) The focus of interpretations has been on the differing electrical resistivities of the phases present, but variations in the magnetic properties may also induce interactions with applied electrical fields. This subject is ripe for study.

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