

Article

## An Entropy-Based Damage Characterization

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**Abstract:** This paper presents a scientific basis for the description of the causes of damage within an irreversible thermodynamic framework and the effects of damage as observable variables that signify degradation of structural integrity. The approach relies on the fundamentals of irreversible thermodynamics and specifically the notion of entropy generation as a measure of degradation and damage. We first review the state-of-the-art advances in entropic treatment of damage followed by a discussion on generalization of the entropic concept to damage characterization that may offers a better definition of damage metric commonly used for structural integrity assessment. In general, this approach provides the opportunity to described reliability and risk of structures in terms of fundamental science concepts. Over the years, many studies have focused on materials damage assessment by determining physics-based cause and affect relationships, the goal of this paper is to put this work in perspective and encourage future work of materials damage based on the entropy concept.

**Keywords:** irreversible thermodynamics; entropy generation; materials damage; structural integrity

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### 1. Introduction

Most structures, such as airframes, naval, and mechanical and civil structures, experience materials damage and accumulate degradation over their lifetime. Failure will eventually occur if the structural

integrity is not adequately managed. Mechanistic-based methods that form the basis for modeling and analysis of structural reliability have been largely unchanged for decades, and most involve considerable uncertainties and conservatisms. Consequently, a more realistic, high-confidence prediction of the behavior of degrading structural materials, both at the micro- and macro-levels, requires a great deal of further fundamental work. It is safe to conclude that a significant gap exists between the available structural integrity technologies and the science of materials degradation dynamics used for modeling early failure prediction, formal development of accelerated failure testing, and prediction of remaining useful life of critical structures. This paper outlines a consistent framework for damage and structural degradation based on the laws of thermodynamics. Within this framework, accumulation of damage will be treated as a dissipative (*i.e.*, irreversible) process that must obey the laws of thermodynamics. Within this framework, accumulation of damage will be treated as a dissipative (*i.e.*, irreversible) process that must obey the laws of thermodynamics.

Aging due to degradation tends to return highly organized structures back to their natural states and reduces the integrity of structural material properties to the point that the structure is no longer sound. An immediate question that arises is how to characterize the deterioration of integrity. Alternatively, what is an appropriate measure of materials degradation? The term “damage” is widely used for this purpose in various disciplines, and in this paper we use this term. The Oxford Dictionary defines damage as “physical harm that impairs the value, usefulness, or normal function of something”. In the engineering context, damage can be thought of as a manifestation of external forces in the form of gradual alteration of matter or dissipation of energy. The forces may be mechanical, thermal, electrical, chemical or their combinations. For example, damage in a structure under fatigue loading manifests itself in forms of cracks, voids and defects. The process of damage in crystalline materials and in polymers may be considered as a chemical reaction in which the composition remains constant, but the bonding structure of the atoms changes [1,2]. Such a process in the presence of repeated mechanical loading even for small amplitude can greatly reduce life of the metals.

Fatigue damage can also be defined according to scale, from the nanoscale through the macroscale. At the nanoscale, the grain boundary, where atoms are more loosely packed, is a likely location for damage. Therefore, at this scale the states of material damage are physically determined by the configuration of the atomic bonds [1]. At the microscale level, damage is the accumulation of the slip irreversibilities that results in strain localizing in a small region within the materials, *i.e.*, persistent slip bands and dislocation cells/bundles [3]. At the mesoscale level, damage is the growth and coalescence of microcracks that initiate a crack. At the macroscale level, damage is the growth of macrocracks that results in final fracture of the structure. The point here is that cause and effect studies of material damage require a sufficiently long stretch of scaling such that nanoscale data can be brought up to the macroscopic scale.

Clearly, the definition of damage varies at different geometric scales as the observable field variables describing the damage change. Furthermore, defining an appropriate damage metric has additional conceptual challenges when dealing with different degradation mechanisms. For example, materials removal owing to friction may be viewed as a measure of damage in tribological systems, while in electrochemistry the change of impedance due to cathodic and anodic polarization may be used as a measure of damage. Therefore, the question arises as to whether a more consistent definition

and theory of materials damage is plausible. In what follows we elaborate on the concept of materials damage and a thermodynamic-based answer to this question.

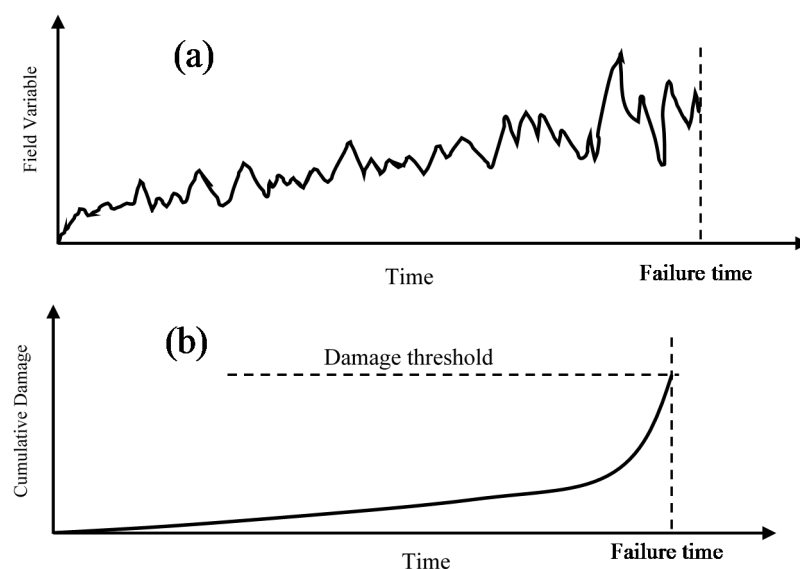
Because the concept of damage is an abstract notion, its definition is relative to a reference state, damage metrics are related to subjective choices of measurable variables. That means damage in this context is the characterization of the observable symptoms in the form of measurable field variables such as crack length, amount of wear, and degree of deformation [4]. Arson [5] states that damage prediction relies on the field variables chosen to describe the anticipated degradation or aging. Singpurwalla [4] refers to these subjective choices of observable field variables as “observable markers”. Even for a single degradation mechanism there may be multiple definitions of damage. For example, fatigue damage has been described as a reduction in the Young’s modulus, as a cumulative number of cycles ratio, as a reduction of load-carrying capacity, as crack length, and as released strain energy.

Thermodynamically, however, all damage mechanisms share a common feature at a much deeper level, which is dissipation of energy. Degradation processes are irreversible, meaning that they cause permanent (irreversible) alteration to the system and the surroundings. Dissipation is a fundamental measure of irreversibility and is common in natural phenomena, including chemical reactions, plastic deformations, frictions, and releases of heat. Dissipation can be quantified by entropy generation. Therefore, dissipation (or equivalently entropy generation) can be regarded as an alternative representation of cumulative damage. Based on this hypothesis, it follows that:

$$\text{Damage} \equiv \text{Dissipation} \quad (1)$$

Note that while damage may be generally described as dissipation, it can still be limited to particular measurable field variables such as crack length or worn material. Later, we suggest that damage can be scaled through a transformation index to an expression of an observable field variable. Thus, damage is a scalar function representing the evolution of a material’s microstructure. The second law of thermodynamics asserts that dissipation is a non-decreasing function, and according to Equation (1) the accumulation of damage is also a non-decreasing function. However, the temporal evolution of observable field variables may fluctuate around some mean value. This is schematically shown in Figure 1.

**Figure 1.** (a) Evolution of observable field variable and (b) evolution of damage accumulation.



Since damage rate in Equation (1) is equivalent to dissipation, we formulate it as a path dependent thermodynamic potential function. The analytical expression of the dissipation potential (or equivalently damage rate potential) is not of concern in this paper. Rather, this paper intends to put forward a general way to quantify damage for different degradation phenomena. As stated by Lemaitre and Chaboche [6], expressing dissipation potential is necessarily a dynamic thinking process that requires the choice of a minimum number of variables necessary to describe the observed phenomena. Depending on the phenomena that are to be modeled under specific conditions, the necessary variables to describe the dissipation potential must be identified by quantitative experiments. Once the dissipation potential is identified, constitutive Equations can be derived. There is no universal way of defining the dissipation potential that implicitly includes constitutive Equations. Depending on the modeler's experience and prior knowledge of the constitutive Equations, it is quite practical to work backwards and get the dissipation potential from the constitutive Equations. Lemaitre and Chaboche [6] presented a comprehensive discussion on the general ways of deriving the constitutive Equations for various degradation phenomena.

In a thermodynamics treatment of irreversible processes, dissipation is quantified by the entropy generation through generalized thermodynamic forces  $X_i$ , and thermodynamic fluxes  $J_i$ ,  $i = 1, \dots, n$ . The index  $i$  refers to the number of different processes,  $p_i$ , acting on the system. Onsager [7] showed that when the fluxes are small and the thermodynamic forces vary slowly, the rate of entropy generation is linearly related to the flows. A major task in developing the proposed damage framework is to properly identify dissipative processes  $p_i$ , the appropriate set of fluxes, and the conjugate driving forces. For example, damage in the corrosion-assisted fatigue damage mechanism is produced by the synergy between two irreversible fluxes: the anodic dissolution current density and the dynamic plastic deformation. Gutman [8] first identified this synergy as the mechanochemical effect, which is the change of physical-mechanical properties and the fine structure (plastic deformation) of a solid under the effect of chemical (electrochemical) reactions on its surface, causing an additional dislocation flow. In this case, entropy generation is the summation of entropy generation due to electrochemical reaction and plastic deformation. The product of a pair of forces and fluxes  $d_i S/dt = X_k J_k$  constitutes a measure of entropy generation ( $d_i S/dt$ ) where summation over  $k$  is applied. As an example, the chemical affinity  $X = A/T$  and the reaction velocity  $J = v$  are the thermodynamic force and thermodynamic flux in a single chemical reaction, respectively. Therefore, the entropy generation is the inner product of these two quantities,  $d_i S/dt = Av/T$  [9]. The thermodynamic forces and fluxes can be scalar, vector or tensor. A detailed discussion of this concept is given in Section 3 of this paper.

The benefit of employing thermodynamic forces and fluxes to characterize materials damage is that the entropy generation can be explicitly expressed in terms of physically measureable quantities such as stress and electrochemical affinity of the oxidation-reduction electrode reaction of a metal ( $\text{Me} \rightleftharpoons \text{Me}^{z+} + ze^-$ ) in the case of the corrosion-fatigue mechanism. Thermodynamics allows for quantifying every dissipative process in the system that gives rise to the entropy generation, irrespective of the underlying degradation phenomena. It also provides a useful technique for studying the synergistic effect from the interaction of two or more processes [8,10].

In this paper, we seek an answer to the question of how the entropy generation can represent the amount of materials damage. Or, put in another way, how can information obtained from thermodynamics be used as an index of damage? The paper is organized as follows: in Section 2, a

brief review of available works on thermodynamic treatment of materials damage is presented. In Section 3, the necessary thermodynamics background for development of a damage theorem is discussed with some examples of damage phenomena studied within the proposed context, followed by conclusions in Section 4.

## 2. Review of Relevant Works

Although the concept of entropy generation for the study of degrading processes is not a new approach and has a rich history of research in chemistry, materials science and mechanics, its application to practical problems is new. A comprehensive review of the application of the concept of entropy in various research areas is given in Martyushev and Seleznev [11]. Entropy can be used in a fundamental way to quantify degradation, including tribological processes such as friction and wear [12–27]. Similarly, other forms of degradation such as fretting [28] and fatigue damage of materials are consequences of irreversible processes that tend to increase the entropy generation of in the material [29–45]. Dissipative processes can be directly linked to thermodynamic entropy, or associated thermodynamic energies, for example plasticity, dislocations [7,46], erosion-corrosion [9], wear-fracture [47,48], fretting-corrosion [49], high current density, thermal gradient, stress gradient and chemical gradient [50,51], thermal degradation, and associated failure of tribological components. Feinberg and Widom [52,53] have related material or component parameter degradation to the Gibbs free energy and predicted that change in the system characteristic results from a log-time aging behavior versus time. This is true only if the damage accumulates at a fixed rate, which assumes constant use and accumulation of damage at a constant rate.

Specifically in fatigue and fracture community, early attempts at entropy based modeling date back to the works of Whaley *et al.* [29–33] who postulated that the entropy generation during fatigue is related to the plastic energy dissipation and can be estimated by integrating the plastic energy per unit temperature of material. It is hypothesized that the total entropy gain due to irreversible plastic deformation can be viewed as a material constant at the onset of fatigue failure. Similarly, Ital'yantsev [54,55] claimed that the fatigue failure occurs when the accumulation of entropy reaches a critical value. He proposed mathematical conditions for failure and showed that the entropy of a material tends to increase until failure occurs, after which the entropy generation vanishes. However, Whaley *et al.* [29–33] and Ital'yantsev [54,55] did not offer experimental observations or quantification of entropy accumulation to support this claim.

Basaran *et al.* [36–41] introduced a damage model described in terms of entropy on the basis of the second law of thermodynamics. They quantified the entropy generation and invoked the Boltzmann statistical entropy to define the isotropic damage evolution function for the eutectic Pb/Sn solder alloys. The model used a small-strains small-displacements assumption with application to electronic packaging. However, in their development of the damage model, Basaran *et al.* treated the interchange between the total entropy,  $S$ , and the entropy generation  $d_iS/dt$ , unclearly and also the model was restricted to small-strain and small-displacement under isothermal conditions. In a similar fashion, Tucker *et al.* [43–44] used the entropic concept for modeling damage and fatigue fracture initiation and growth in solder joints. A fracture model was also derived from concepts of information theory and statistical thermodynamics based on the Maximum Entropy Production Principle (MEPP).

However, in their fracture models Tucker *et al.* [43–44] did not make a clear distinction between the total entropy and the entropy generation, which are two different quantities. Recently, Ontiveros *et al.* [56] utilized entropy generation to predict time of fatigue crack initiation in notched specimens undergoing uniaxial cyclic load. Their experiments pertained to fatigue testing of aluminum alloy 7075-T651 to determine the applicability of the entropy generation as an index of crack initiation. Results of their work suggest that time for short fatigue crack can be estimated via cumulative entropy generation, and that is not only a function of the cumulative entropy generation but also a function of the likelihood of microcrack formation.

Thermodynamic treatment of wear damage has also been extensively studied. Early attempts date back to the work of Klamecki [11–14] who performed a near-equilibrium analysis via entropy generation to demonstrate energy dissipation in friction processes. Klamecki showed that entropy could be used to describe all dissipative processes in sliding contact, including wear damage. Experimental work of Doelling *et al.* [18] showed that amount of mass removal due to wear is linearly correlated with entropy flow. Entropy flow was calculated by means of a calorimeter via measuring heat generation and temperature rise at contact surfaces. They also showed that the classical Archard's wear law is a thermodynamic consequence and thus is subsumed in their generalized functional relationship between wear and entropy flow. It is to be noted that the work of Doelling *et al.* [18] pertained to steady-state condition where entropy flow is equal to entropy generation (see Section 3). In fact, it is entropy generation that represents exhaustion (degradation) of a thermodynamic system. However, experimental measurement of entropy flow is simpler than entropy generation and merely requires measuring entropy due to heat and mass exchange with the environment. Several other studies are available on thermodynamic assessment and specifically entropic assessment of tribosystems (e.g., [15–17,19–24,28,57]). Amiri and Khonsari [26] provide a comprehensive review of the entropic approach to friction and wear problems.

The preceding literature review supports that the concept of entropy may provide a relatively general modeling approach to a wide range of damage processes with promising results in fracture mechanics and fatigue damage analysis of engineering materials, tribology and mechanochemical processes. However, further work is needed to formally construct a generalized entropic damage model that adequately explains single materials' damage mechanism as well as the synergistic effect between different mechanisms. Bryant *et al.* [58] have made attempts towards this generalization to establish a general relationship between the degradation of systems undergoing irreversible dissipative processes and the simultaneous entropy generation. They formulated the Degradation-Entropy Generation (DEG) theorem and applied it to a system with a single dissipative process. Their work was focused on processes involving friction and wear. No detail is given on how the synergism of multiple dissipative processes can be addressed within the entropic theorem. Furthermore, the definition of damage and its measure for different processes are not discussed in their work. This paper extends the DEG theorem to address these concerns.

### 3. Thermodynamic Treatment of Materials Damage

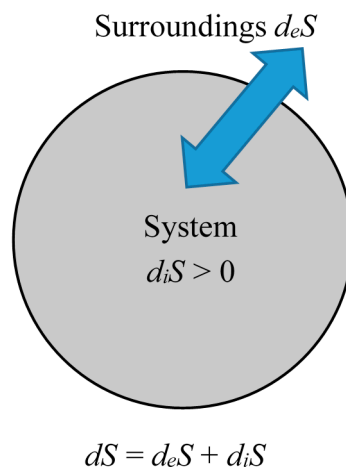
#### 3.1. Fundamentals of Irreversible Thermodynamics

A description of the irreversible processes requires formulating the first and the second laws of thermodynamics as applicable to a system whose properties are continuous functions of space and time (Figure 2). In a system that involves chemical reaction and work of any form, the change in internal energy  $U$  can be formulated on the basis of combining the first and second laws as:

$$dU = TdS + \delta W + X_i d\xi_i + \mu_k dN_k \quad (2)$$

where  $\delta W$  is the mechanical work in the bulk of the system (work of deformation),  $TdS = \delta Q$  is the amount of heat introduced into the system from the environment in a reversible process,  $X_i$  is generalized force (such as pressure) and  $\xi_i$  is the generalized coordinate (such as volume),  $\mu_k$  is the chemical potential and  $N_k$  is the number of moles of  $k$ -th species. The summation convention is applied to Equation (2).

**Figure 2.** Entropy balance for a system.



The time derivative of Equation (2) can be written in the following form:

$$\dot{U} = T\dot{S} + \dot{W} + X_i J_i + \mu_k v_k \quad (3)$$

where  $J_i = d\xi_i/dt$  and  $v_k = dN_k/dt$ . Note that  $\dot{W}$  in Equation (3) is associated with the work of quasi-conservative forces and  $X_i J_i$  is associated with the work of dissipative forces. In fact, forces applied on the system can be divided into quasi-conservative and dissipative forces as discussed by, for example, Ziegler [59–60]. Quasi-conservative forces are derivable from free energy and do not contribute to dissipation.

The work of external forces can be attributed to electrical, magnetic, radiation or any other external fields acting on the system. Note that in Equation (2), change of kinetic energy and potential energy is neglected, as it is a good approximation in most damage processes. To account for irreversible processes, the second law of thermodynamics can be introduced as [8]:

$$dS = d_e S + d_i S; \quad d_i S > 0 \quad (4)$$

where  $d_e S$  is the entropy exchange (flow) with the surroundings and  $d_i S$  is the entropy generation inside the system (see Figure 2). The  $d_i S/dt$  represents internal irreversibility (dissipation) in the system. In addition to heat exchange, the system may exchange mass with the surroundings (*i.e.*, in an open system such as in wear and corrosion). The entropy exchange (also known as entropy flow) can be positive, negative or zero. In case  $d_e S = 0$ , the system does not exchange heat and mass with the surroundings and the entropy flow is zero. Therefore, in Equation (2)  $dN_k$  for an open system consists of mass change due to chemical reaction  $d_i N_k$  and mass transport term  $d_e N_k$ ; *i.e.*,  $dN_k = d_i N_k + d_e N_k$ .

Equation (4) can be expressed in a more useful form. Under the hypothesis of local equilibrium the entropy balance Equation (4) can be expressed in local form as:

$$\rho \frac{ds}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma \quad (5)$$

where

$$S = \int_V \rho s dV$$

$$\frac{d_e S}{dt} = - \int_{\Omega} \mathbf{J}_s \cdot d\Omega$$

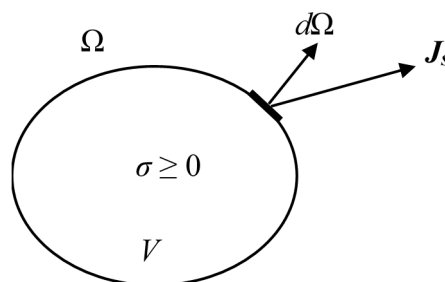
$$\frac{d_i S}{dt} = \int_V \sigma dV$$

where  $s$  is the entropy per unit mass,  $\rho$  is the density,  $\mathbf{J}_s$  is the total entropy flow per unit area and unit time,  $d\Omega$  is the element of surface area (see Figure 3), and  $\sigma$  denotes the entropy generation per unit volume per unit time. The second law of thermodynamics requires

$$\sigma \geq 0.$$

Note that we used notation  $\sigma$  for the volumetric representation of entropy generation  $d_i S/dt$ .

**Figure 3.** Entropy generation and entropy flow for a system.



The concept of local equilibrium simply assumes that for a thermodynamic system, intensive variables such as temperature and pressure can be well defined locally: *i.e.*, over small but still macroscopic regions. Based on this assumption, systems may be globally not in thermodynamic equilibrium, but still remain in local equilibrium. Systems at thermodynamic equilibrium attain maximum entropy. At equilibrium all thermodynamic fluxes vanish, which results in zero entropy generation rate,  $\sigma = 0$ . Therefore, the necessary condition for thermodynamic equilibrium can be expressed as [61]:



$$X_i = J_i = 0. \quad (6)$$

Thermodynamic fluxes determine the dissipative trait of processes. This means if all thermodynamic fluxes are zero, the process is non-dissipative, which results in thermodynamic equilibrium condition as stated in Equation (5).

The entropy generation rate per unit volume within the system,  $\sigma$ , is always positive and characterizes expenditure of the system's life. Accordingly, the damage rate of the system is intimately connected to the entropy generation that accumulates progressively over time and degrades the system until its final breakdown [45,58]. Therefore, in order to assess damage induced in the system, we should identify the thermodynamic forces and fluxes for every fundamental dissipative process active in the system. This subject will be discussed in detail later in this section. In the thermodynamics of irreversible processes,  $\sigma$  can be expressed in terms of thermodynamic forces and fluxes as:

$$\sigma = X_i J_i \quad (7)$$

Note that the summation convention is automatically applied to Equation (7) and  $\sigma$  is the volumetric entropy generation rate. In general, thermodynamic fluxes depend not only on their conjugate force but also on all other forces. This is due to the synergistic effect that might exist between different dissipative processes. Therefore Equation (7) can be written as:

$$\sigma = X_i J_i (X_j); \quad (j = 1, \dots, n) \quad (8)$$

In the case of spatial symmetry properties in the system, Cartesian components of the thermodynamic fluxes do not depend on all the Cartesian components of the thermodynamic forces; this is known as the Curie Principle [62] (p. 57).

To better understand the thermodynamics of materials damage, let us briefly elaborate on some fundamental concepts. First, we must note that all degradation mechanisms leading to damage are non-equilibrium, meaning that they evolve in time and/or space, and there is one or more non-vanishing flux in the system. In equilibrium, all fluxes vanish. In fact, the equilibrium thermodynamic deals with the initial and final states of the system without specifying information about how the system evolves between these two states. The non-equilibrium thermodynamic, on the other hand, provides the mathematical tool to study the evolution of the system's properties in the course of time and space, which is the case in the degradation processes considered here. However, the degradation processes that we consider are relatively slow phenomena that occur over a long period. For example, consider the corrosion damage of a reinforced concrete structure with the timescale measured in decades. Therefore, for such processes the *local equilibrium* hypothesis is justified. According to Lebon *et al.* [63] the local equilibrium hypothesis states that the local and instantaneous relations between a system's properties are the same as for a uniform system in equilibrium. We divide the system into cells that are sufficiently large for microscopic fluctuations to be negligible but sufficiently small so that equilibrium is realized to a good approximation in each individual cell. Based on the local equilibrium hypothesis, each cell is assumed to be in equilibrium state. Thermodynamic properties are uniform within each individual cell, but can be different among the neighboring cells. Also, in each individual cell equilibrium state can change with time [63]. Moreover, two timescales can be considered to check the applicability of the local equilibrium assumption. The first timescale,  $t_m$ , is the time that an individual

cell attains equilibrium state, and it is of the order of the time interval between two successive collisions between particles: *i.e.*,  $10^{-12}$  s, at normal pressure and temperature. The second timescale,  $t_M$ , is related to the time required for macroscopic change of the system. This may be the time required for macroscopic damage induced in the system, or may be related to the duration of an experiment. The ratio of these two timescales is called the Deborah number (*i.e.*,  $De = t_m/t_M$ ). For  $De \ll 1$ , the local equilibrium hypothesis is applicable because the relevant variables evolve on a large timescale  $t_M$  and do practically not change over the time  $t_m$ , but the hypothesis is not appropriate to describe situations characterized by  $De \geq 1$ . Large values of  $De$  are typical of systems with long relaxation times, like polymers, for which  $t_m$  may be of the order of 100 s, or of high-frequency or very fast phenomena, such as ultrasound propagation, shock waves, nuclear collisions, for which  $t_M$  is very short, say between  $10^{-5}$  and  $10^{-10}$  s [63]. Therefore, for the degradation processes considered in this work, the hypothesis of local equilibrium is justified.

Another important topic relevant to the present discussion is possible existence of the general extremal principle that governs the evolution of a non-equilibrium system. Perhaps MEPP, also known as Ziegler's principle [59], provides the “easiest and most accessible” [64] evolution of a non-equilibrium system. Fundamental studies available in the literature show its successful applications for description of non-equilibrium problems. Martyushev and Seleznev [10] presented a comprehensive review of these studies, which simply states that *if thermodynamic forces  $X_i$  in Equation (6) are preset, then thermodynamic fluxes  $J_i$  evolve such that the entropy generation rate  $\sigma$  is maximized*. If entropy generation rate  $\sigma(\mathbf{J})$  is defined in flux space, then MEPP yields the explicit relation between thermodynamic forces and fluxes as follows:

$$X_i = \lambda \frac{\partial \sigma}{\partial J_i} \quad (9a)$$

where the proportionality factor  $\lambda$  can be obtained from Equation (7) as:

$$\lambda = \frac{\sigma}{(\partial \sigma / \partial J_i) J_i} \quad (9b)$$

where summation over  $i$  is applied. In using MEPP via Equation (9), fundamental points relevant to its region of applicability must be considered [65]. Forgetting these fundamental points has raised several questions about the validity of MEPP and therefore, misconceptions. Some of the critical discussions on validity and applicability of MEPP can be found in [67–71]. Martyushev and co-workers in several publications [64–66] have clarified the region of applicability of MEPP and enumerated its restrictions. Out of six restrictions that Martyushev [66] has enumerated, we briefly discuss two that we believe are most important. One restriction is that MEPP is based on the local equilibrium hypothesis, meaning that the thermodynamic forces in Equation (9a) are determined from maximization of entropy generation in a sufficiently small subsystem. The other restriction is that MEPP holds for coupled (complex) processes. Complex processes consist of more than one elementary process, and thermodynamic flux of elementary process depends not only on its conjugate force but also on other forces [59]. Therefore, various elementary processes are coupled. On the other hand, if thermodynamic forces of various elementary processes only depend on their conjugate force, the elementary processes are uncoupled. Ziegler refers to this process as compound. This restriction, which is often forgotten, is clearly pointed out by Ziegler [59] (pp. 259–261). For completeness of our discussion, let us quote Ziegler's comment,

“The orthogonality condition [MEPP] need not hold for the compound process; however, when applied to the various elementary processes, it yields all of the dissipative forces.” For a special case in which entropy production generation of a compound process takes the form of homogeneous function of degree  $r$ , the MEPP can be applied to the entire system [59] (pp. 261–262). It is therefore possible that discounting these restrictions may lead to a misconception of MEPP.

If we start with the hypothesis that dissipation potential (or equivalently entropy generation) is metric for damage and thus a scalar damage function,  $D$ , it may be defined depending on the same dissipative processes  $p_i$  that give rise to the entropy generation. It follows that the corresponding entropy generation  $(XJ)_i$  may be scaled through a transformation index to an expression of damage function. That is, the damage function is a transformation of the entropy generation from the thermodynamics context to the damage context through a scaling transformation index, referred to as degradation coefficient [58]. Degradation coefficient  $B$ , which depends on the degradation process, in a system consisting of only one dissipative process  $p$ , for example, transforms the entropy generation  $\sigma = XJ$  to the damage function describing the rate of damage as  $D = BXJ = B\sigma$ . A corollary is that the total amount of damage is a linear combination of the total components of entropy produced by the dissipative processes  $p_i$ . It is to be noted that the entropy generation  $\sigma$  has a unit of Watts per Kelvin per cubic meter [ $\text{W}/(\text{m}^3 \text{ K})$ ], while the dimension of the rate of damage  $D$  depends on the observable variables chosen by the modeler. For instance,  $D$  in fatigue can be defined as the rate of change in Young’s modulus  $D = dE/dt$  with dimension of [ $\text{N}/(\text{m}^2 \text{ s})$ ] that results in dimension of [ $(\text{N K m})/(\text{W s})$ ] for degradation coefficient. The dimension of the degradation coefficient is not unique and varies based on the choice of damage  $D$ .

In general, if  $n$  dissipative processes are active in the system,  $p_i$ ,  $i = 1, \dots, n$ , the total damage would be the summation of the damage attributed to each dissipative process alone (*i.e.*,  $D = D_1 + \dots + D_n$ ). This can simply be proved as a consequence of the linear relationship between the entropy generation and the damage. We note that, in general, synergistic mechanisms may exist for which damage of one mechanism  $D_i$  may be influenced (accelerated or decelerated) by other mechanisms  $D_j$  ( $i \neq j$ ). In real damage processes, it is commonly observed that one or more of the components of entropy generation dominate the total entropy generation. Therefore, the effect of the remaining components on damage can be neglected. For example, in high-cycle fatigue, entropy generation due to heat transfer is insignificant compared to entropy generation by stress, and thus its effect on damage can be neglected. To develop the generalized thermodynamics framework for damage, each component of damage is mapped into a component of entropy generation; however, the opposite of the statement is not necessarily true, meaning that each component of entropy generation may not individually be realized as damage.

In what follows, we present microstructural analyses of the key damage features for metals under various degradation mechanisms. Microstructural aspects of cause of damage for some familiar degradation mechanisms such as fatigue damage, corrosion damage, radiation damage, creep damage and wear damage are discussed. The following discussion is an attempt to describe damage in thermodynamic context by giving some examples and is, by no means, a comprehensive description of underlying mechanisms of damage initiation and growth. It is therefore not an objective of this paper to discuss the physics-based cause and effect relationship of materials damage. Many studies have focused on this phenomenon over the years and the goal of this paper is to put this work in perspective and encourage future work of materials damage based on the entropy concept.

### 3.2. Microscopic Origin of Materials Damage

In general, damage can be envisaged as either surface deterioration or volumetric deterioration of material. For example, fatigue and creep are processes that cause damage to volume elements of a structure, while corrosion and wear cause surface damage. It is, of course, possible for a combination of these processes to cause simultaneous surface and volumetric damage. Therefore, definition of damage and its mathematical representation must be general enough to encompass both categories as well as their combination. At the macroscopic scale, realization of material damage becomes difficult and very much dependent on the type of damage, whether internal or surface damage. For example, pitting corrosion is a form of localized surface damage leading to pits of small or large diameters, deep or shallow, undercut, close to each other or isolated. According to Davis [72], pitting corrosion is one of the most difficult forms of corrosion damage to detect because it can cause only a small mass loss which, if small in size, can be easily overlooked. Similarly, there is no general measure or model to assess volumetric material damage. Lemaitre and Chaboche [5] (p. 348) state that “[t]here is nothing (almost nothing!) that macroscopically distinguishes a highly damaged volume element and a virgin one.” Therefore, unless observable features of damage such as discontinuity, permanent distortion, discoloration of the material can be observed, it would be difficult to assign a state of damage to the volume element of the material. Once macroscopic damage is observed, catastrophic failure is often imminent.

It is, therefore, a fair statement that a systematic procedure for defining and evaluating damage is not available. Rather, practitioners have used “symptoms” of damage such as crack size and changes of physical and mechanical properties of material instead. For example, density of cracks and defects may be measured at the microscopic scale and be integrated over the macroscopic volume element using mathematical homogenization techniques [5] (p. 348). Also, measurements of any change in resistivity of physical properties such as thermal resistivity, electrical resistivity, acoustic and magnetic resistivity are common techniques to evaluate damage. In this case, a predefined threshold for the change of physical resistivity is considered an indication of failure. Also, changes in mechanical properties such as reduction of the elastic modulus, accumulation of plastic strain, or change in viscoplastic properties are other indications of damage accumulation.

Difficulty that arises in defining a physically and geometrically consistent representation of damage at the macroscopic scale has compelled researchers to look for a microscopically consistent definition of material damage. At the micro- and sub micro-scales, however, material damage can be defined in a more coherent way. In fact, at the nano-scale, damage may refer to breaking and reestablishing of interatomic bonds in crystalline metals and polymers [1]. When applied on the material, external load causes atoms to be displaced from their equilibrium position. In this irreversible process, previous interatomic bonds break, reestablish new bonds, and move to new equilibrium states. Based on this fundamental definition of damage, meso-scale characteristics of damage such as dislocations, slips, microcavities, and microcracks can be quantified. Interested readers may refer to Woo and Li [1] for detailed discussion.

Over the course of past decades, the impact of computation on damage simulation has expanded dramatically. In fact, the promise of multiscale damage modelling and simulation has greatly enhanced our understanding of damage mechanisms from atomic scale up to macroscale. However, what still remains a challenge is how the understanding of mechanisms at the microscale can enable predictions

of functional behaviour at the macroscale. In other words, bridging the gaps between different length and time scale still remains a challenge. In the remaining sub-sections, we will discuss micro- and macro-scale characteristics of damage mechanisms in some commonly observed failure modes such as fatigue, corrosion, creep, wear, irradiation, and thermoelectric migration. Accordingly, the thermodynamic theory of irreversible processes is adopted to describe the damage process in terms of dissipation and entropy generation.

### 3.3. Fatigue Damage

Fatigue process in generic engineering alloys is manifested by the cumulative degradation at different length scales, from atomistic dislocation nucleation at material's grain boundaries to visible macro-scale crack propagation. It is widely accepted among the research community that the dissipative feature of materials during deformation can be attributed to dislocation. The origin of this notion dates back to the pioneering work of Eshelby [73], who explained the mechanism of energy dissipation in metals for the first time based on the concept of dislocation. Using the theory of internal friction introduced by Zener [74], Eshelby described the mechanism of mechanical damping in vibrating metals as he incorporated the role of moving dislocations on damping. He postulated that in addition to thermoelastic damping (e.g., in Zener's case), there is an additional energy loss due to the oscillation of dislocations. The motion of dislocations leads to redistribution of stresses in the material which, in turn, results in temperature change at any locations. The resulting temperature gradient drives the heat flow and causes mechanical damping. This damping depends on applied stress and density of the dislocations.

In this section we discuss a simple dislocation model to explain fatigue plasticity in engineering alloys and its representation in entropic context. Sophisticated models and simulation techniques such as molecular dynamics, micromechanical approaches, crystal plasticity, etc. have been developed by researchers over the past decades in order to gain a fundamental understanding of the effects of cyclic loading on fatigue damage accumulation. Discussion of the underlying mechanism of fatigue damage accumulation and crack initiation is beyond the scope of this paper. Interested readers may refer to a comprehensive review by Sangid [3] and discussions by Mughrabi [75] and McDowell and Dunne [76] Gomez and Basaran [79,83] and other works [77–81]. Let us assume that fatigue damage is caused by plastic deformation of bulk material. Even if bulk stress and strain are in the elastic region, in the vicinity of inherent micro defects deformation can be locally plastic. In fact, defects developed initially at atomic level due to cyclic slip and grow to form microscopic fatigue damage commonly known as microplasticity [75] that accumulates irreversibly to form micro- to macro-cracks. During plastic deformation, dislocations nucleate and move simultaneously. Using Orowan's Equation [84] the plastic shear rate  $\dot{\gamma}_p$  is related to the magnitude of the Burgers vector,  $b$ , the dislocation density,  $N$ , and the velocity of mobile dislocations,  $V$ , as [8]:

$$\dot{\gamma}_p = NbV \quad (10)$$

In case of uniaxial stress under the assumption of homogeneous strain, Kelly and Gillis [85] have shown that the plastic strain rate  $\dot{\epsilon}_p$  can be written as:

$$\dot{\epsilon}_p = \mu f \dot{\gamma}_p = \mu f NbV \quad (11)$$

where  $\mu$  is an orientation tensor and  $f$  is mobile fraction of dislocation. The next step is to evaluate dislocation velocity,  $V$ . Numerous functions have been suggested to represent  $V$  as a function of the stress  $\sigma$ . Kelly and Gillis [85] suggested a simple function as:

$$V = V_0 \left( \frac{\sigma}{\sigma_0} \right)^n \quad (12)$$

where  $V_0$  is the average dislocation velocity at stress  $\sigma_0$ . The exponent  $n$ , average velocity  $V_0$ , and stress  $\sigma_0$  are the material's characteristics. Therefore the plastic strain rate is:

$$\dot{\epsilon}_p = \mu f N b V_0 \left( \frac{\sigma}{\sigma_0} \right)^n \quad (13)$$

Equation (13) is similar to the plastic part of the Ramberg-Osgood relationship [86]. In the context of irreversible thermodynamics discussed in Section 1, rate of plastic strain constructs thermodynamic flux  $J = \dot{\epsilon}_p$  driven by the applied stress as the thermodynamic force  $X = \sigma$ . In general, the rate of plastic strain and stress are second-order tensors. We denote tensors with bold face characters. We, therefore, can express the dissipation, or equivalently the entropy generation, of the plastic deformation in the following form:

$$\phi = T \frac{d_i S}{dt} = XJ = \boldsymbol{\sigma} : \dot{\boldsymbol{\epsilon}}_p \quad (14)$$

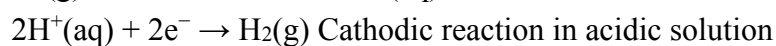
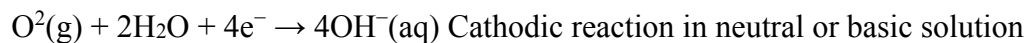
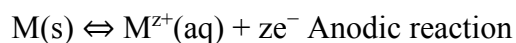
The entropy generation given by Equation (14) is, in essence, a measure of damage in the process of formation and movement of dislocations in plastic deformation. As mentioned earlier, the formation and movement of dislocation dominate the fatigue damage mechanism. Therefore, entropy generation is rationally an indication of fatigue damage. It is to be noted that Equation (14) merely includes dissipation due to strain energy of the hysteresis effect, while in a fatigue process several dissipation sources may exist as well. These can be listed as heat conduction, kinematic and isotropic hardening. Evaluation of dissipation due to plastic deformation requires measurement of stress and rate of plastic strain at any instant in time. Integration of Equation (14) with respect to time results in accumulation of entropy generation which, in turn, is a measure of damage accumulation. Integration of Equation (14) over one fatigue cycle represents hysteresis energy generation that is equal to the area confined in the hysteresis loop. Fatigue tests under controlled laboratory conditions should be performed either under stress controlled or strain controlled condition. If we consider the stress controlled fatigue test, then thermodynamic force is constrained and thermodynamic flux varies in response to the force.

### 3.4. Corrosion Damage

Corrosion is degradation of a material (usually a metal) due to chemical or electrochemical reaction with its environment. Degradation is usually in the form of change in properties and/or material loss from the surface as the metal is dissolved and leaves the surface in the form of ions or some other kind of corrosion products. Therefore, corrosion can be classified as a surface degradation. Corrosion damage can be divided into several categories based on the appearance of the corrosion damage or the mechanism of attack. Jones [87] has classified corrosion damage into nine distinct forms, listed as uniform or general corrosion; galvanic corrosion; crevice corrosion; pitting corrosion; environmentally assisted cracking, including stress corrosion cracking, fatigue corrosion and hydrogen-induced

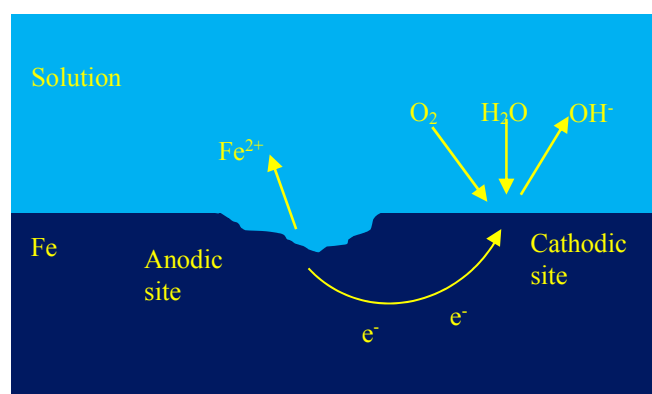
cracking; hydrogen embrittlement; intergranular corrosion; dealloying; and erosion-corrosion, including fretting-corrosion and cavitation-corrosion. In general, the available models for prediction of corrosion degradation can be divided into two groups: (1) approaches that account for assessing corrosion rate (expressed as the corrosion current density,  $i_{corr}$ ), and (2) those that account for assessing corrosion-induced damage (e.g., density and size distribution of pits, stress cracking, loss of stiffness, etc.). The first group of models relies on the fact that when metals come into contact with electrolyte, electric current and electric potential are formed at the metal surface which lead to the formation of cathodic and anodic sites. Intensity of corrosion current density represents a measure of corrosion. Progression of corrosion damage decreases electrical resistance of the solution and thus increases the corrosion current density. Numerous models are available for corrosion damage prediction based on corrosion current density  $i_{corr}$ . Otieno *et al.* [88] present a review of available prediction models for reinforced concrete structures. The second group of models, in contrast, relies on the prediction of the service life of structures defined as the time to corrosion-induced damage such as cover cracking. In order to make accurate and realistic predictions of a structure's service life using the first group of models,  $i_{corr}$  must be accurately measured. This requires real-time monitoring and advanced sensors that can be embedded within the structure during its service life. Due to the practical challenges associated with this technique, more focus has been placed on the prediction of corrosion-induced damage [88]. However, a comprehensive understanding of corrosion damage requires studying the thermodynamics of electrochemistry and irreversibility associated with  $i_{corr}$ .

Let us consider anodic and cathodic reactions for a typical metal  $M$  in an electrolyte. Both reactions occur simultaneously on the metal surface and can be represented as:



Anodic and cathodic reactions occur simultaneously at different locations on the surface. Figure 4 schematically shows the corrosion process that occurs at the surface of iron in basic solution.

**Figure 4.** Electrochemical reaction occurring on the surface of iron in a basic solution (Reproduced from McCafferty [89]).



The entropy generation due to chemical reaction is:

$$\phi = T\sigma = -\mu_i \alpha_{ki} v_k > 0 \quad (15)$$

where  $\mu_i$  is chemical potential;  $v_k$  is reaction rate; and  $\alpha_{ki}$  are the stoichiometric coefficients of reacting substances and products. In general, the chemical affinity  $A_k$  of a reaction can be written in terms of chemical potentials  $\mu_i$  as [9]:

$$A_k = -\mu_i \alpha_{ki} \quad (16)$$

Therefore Equation (16) yields:

$$T\sigma = A_k v_k > 0 \quad (17)$$

In general, the chemical affinity  $A_k$  and reaction rate  $v_k$  can be related through  $v_k = R_{fk} (1 - \exp(-A_k/RT))$ , where  $R_{fk}$  is the forward reaction rate for species  $k$  and  $R$  is the universal gas constant. For near equilibrium condition where  $A_k/RT \ll 1$ , we obtain a linear relationship between  $v_k$  and  $A_k$  as  $v_k = R_{fk,eq} (A_k/RT)$ , where  $R_{fk,eq}$  denotes the equilibrium value of the forward reaction rate [9]. However, corrosion is an electrochemical process that includes an electric field due to anodic reaction in addition to chemical reaction. If we assume anodic reaction results in polarization of an electrode, *i.e.*, change of electrode potential by value of  $\Delta\phi$ , the electrochemical potential can be obtained from De Groot and Mazur [62] (p. 449):

$$\tilde{\mu}_i = \mu_i + zF\Delta\phi \quad (18)$$

where  $F$  is Faraday's constant (96,500 A s) and  $z$  is the ionic charge per unit mass (2 for  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ ). Therefore, the total electrochemical affinity  $\tilde{A}$  is determined by Equation (18), where  $\mu_i$  is replaced by  $\tilde{\mu}_i$  from Equation (18):

$$\tilde{A} = A + zF\Delta\phi \quad (19)$$

Since the phenomena of electrochemistry is accompanied by flow of electric current  $i_{corr}$ , the entropy generation in an electrochemical process can thus be written as:

$$\sigma = \frac{\tilde{A} i_{corr}}{zT} > 0 \quad (20)$$

In the context of irreversible thermodynamics discussed in Section 1, the electric current density constructs the thermodynamic flux  $J = \frac{i_{corr}}{z}$  driven by the total electrochemical affinity as the thermodynamic force  $X = \tilde{A}/T$ .

The corrosion current density  $i_{corr}$  has been extensively used by researchers to model corrosion damage. Several corrosion damage models are available that rely on  $i_{corr}$  as a measure of damage (see, for example, Otieno *et al.* [88]). For example, Stern-Gary's model [90] is applicable to the linear regions of polarization in which slight changes in current applied to corroding metal in an ionic solution cause corresponding changes in the potential of metals. In pioneering work of Stern and Gary [90] for a simple corroding system, the corrosion rate is inversely related to the polarization resistance  $R_p$  as:

$$i_{corr} = \frac{B}{R_p} \quad (21)$$

where  $i_{corr}$  is corrosion current density in A/cm<sup>2</sup>;  $B$  is Stern–Gary constant in V; and  $R_p$  is polarization resistance in  $\Omega \cdot \text{cm}^2$ . The value of  $B$  is determined from the particular electrochemical cell and generally ranges from 13 to 52 mV depending on the system. A value of 26 mV is commonly used for steels embedded in concrete for the active corrosion [91]. Having determined the corrosion rate ( $i_{corr}$ )



from Equation (21) or other available models, metal loss due to corrosion can be estimated. The volumetric loss  $V_{corr}$  (or mass loss,  $M_{corr}$ ) of metal by unit of area and unit of time is expressed in mm/year, or in kg/m<sup>2</sup>-year in the case of mass loss.  $V_{corr}$  is obtained from the corrosion current ( $i_{corr}$ ) through Faraday's law and the density of the metal. For uniform corrosion of steel, for example, 1  $\mu\text{A}/\text{cm}^2$  is equivalent to a rate of metal loss of 0.0116 mm/year [92]. Thus, the volumetric and mass loss of steel due to corrosion can be expressed as:

$$V_{corr} = 0.0116 i_{corr} \quad (22)$$

where  $V_{corr}$  is in mm/year and  $i_{corr}$  is in  $\mu\text{A}/\text{cm}^2$ . Mass loss is:

$$M_{corr} = 9.127 i_{corr} \quad (23)$$

where  $M_{corr}$  is in kg/m<sup>2</sup>-year and  $i_{corr}$  is in  $\mu\text{A}/\text{cm}^2$ . Equations (20–23) show that corrosion damage may be treated within the framework of non-equilibrium thermodynamics by measuring entropy generation in the electrochemical corrosion process.

### 3.5. Wear Damage

Pressing two bodies together and setting the contact in motion is always accompanied by dissipation of energy. The main factor that controls energy generation within the contact of a sliding system is the interfacial friction. The frictional energy generated between contacting bodies is governed by the combination of applied load and velocity. Other contacting factors such as the material properties, relative velocity and size also influence the distribution and dissipation of the frictional energy. Wear damage as a consequence of friction process manifests itself in the form of gradual material removal from interface of two contacting bodies.

There is no wear model derived from fundamental principles for general and practical use. Useful Equations are empirical and suitable for very special materials and conditions. Meng and Ludema [93] analyzed over 180 wear Equations with over 100 variables used in these Equations. They found no way to unify a group of Equations suitable for general use. However, Ludema [94] categorized these Equations into three groups based on typical wear parameters: material parameters, operational parameters and environmental parameters.

Let us consider a simple tribosystem as shown in Figure 5. It consists of two contacting bodies with normal contacting force of  $N$  and relative velocity of  $V$ . For simplicity, consider that one material is softer than the other. Therefore, wear damage occurs due to material removal from the softer body. If  $\mu$  denotes the coefficient of friction, power loss of the frictional force is  $P_{loss} = \mu NV = FV$ , where  $F = \mu N$  is friction force. With simplifying assumptions of no chemical reaction, no diffusion, negligible wear and assuming that at steady-state condition all heat is transferred to the wearing material, the frictional power loss is equated to the heat generation transferred into the wearing material. Therefore,

$$\begin{aligned} Td_e S + Td_i S &= 0 \\ P_{loss} &= -dW/dt = -dQ/dt = -Td_e S/dt = Td_i S/dt. \end{aligned} \quad (24)$$

Therefore, entropy generation due to frictional power dissipation is:

$$\sigma = \frac{d_i S}{dt} = \frac{P_{loss}}{T} = \frac{\mu NV}{T}. \quad (25)$$

Doelling *et al.* [18] experimentally measured entropy generation in Equation (25) for a pair of wearing materials and showed that accumulation of entropy generation is linearly correlated to wear volume. By increasing entropy generation, wear volume increases and vice versa. Equation (25) suggests forms of thermodynamic force and flux in this simplified wear model as:

$$X = \frac{\mu N}{T}; J = V. \quad (26)$$

From a thermodynamics point of view, a tribosystem is, however, more complex than just generating frictional heat. As shown in Figure 5(b), the friction process includes, for example, entropy flow due to mass and heat exchange with the surroundings and entropy generation due to heat conduction. In this case, the entropy balance in Equation (5) can be simply written as:

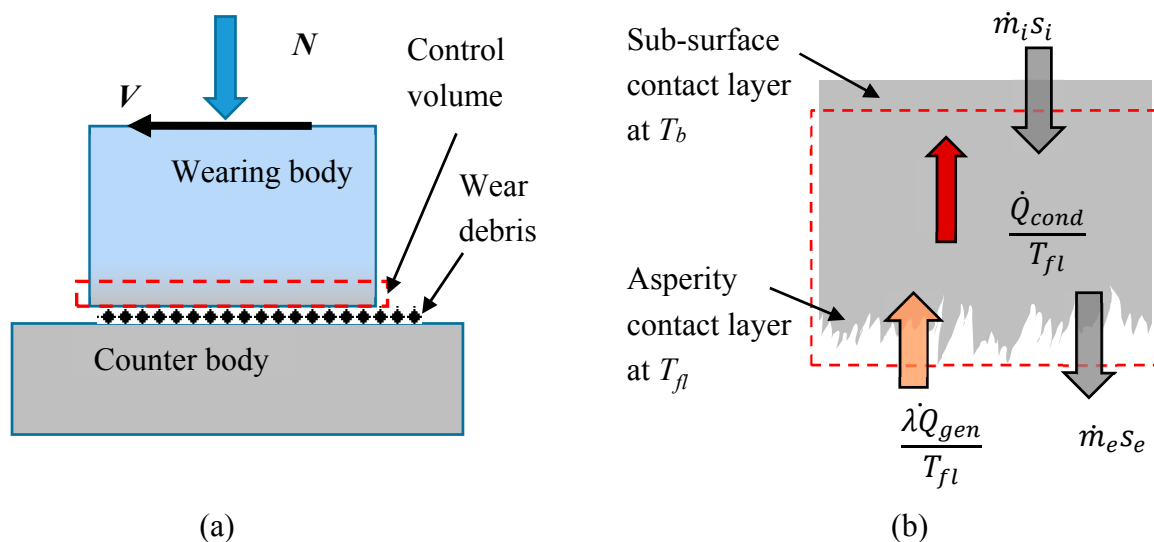
$$\frac{dS}{dt} = \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \sum_j \frac{\dot{Q}_j}{T_j} + \sigma \quad (27)$$

where  $\dot{m}_i s_i$  and  $\dot{m}_e s_e$  are entropy flows entering and exiting the control volume, respectively. It is to be noted that only a fraction of frictional heat generation at interface,  $\dot{Q}_{gen}$ , enters the control volume,  $\lambda \dot{Q}_{gen}$ . The remaining heat will be transferred away from the system by means of wear particles and lubrication. The partitioning factor,  $\lambda$ , depends on the properties of two contacting materials. Readers interested in a formula for  $\lambda$  may refer to the work of Amiri *et al.* [25]. At steady-state condition, Equation (27) reduces to following Equation for entropy generation within the control volume:

$$\sigma = \sum_e \dot{m}_e s_e - \sum_i \dot{m}_i s_i - \sum_j \frac{\dot{Q}_j}{T_j}. \quad (28)$$

Abdel-Aal [24] has evaluated each of terms on the right hand side of Equation (28) in order to evaluate the entropy generation in a tribosystem. In fact, this evaluation requires one to carefully identify all possible means by which entropy can flow in and flow out of the control volume. Comprehensive studies have been done by Abdel-Aal [21–24] to evaluate the strength of the source of the entropy generation and its relation to the amount of wear damage.

**Figure 5.** Schematic of a tribosystem (a) including wearing body and counter body, (b) control volume enclosing interface of dissipative processes, thermodynamic model.



In a more general consideration, Bryant [19] identified prevalent dissipative processes at tribological interfaces and estimated the irreversible entropy generations. In this case entropy generation includes contribution from different dissipative processes such as: (a) adhesion of surfaces and films associated with adhesive wear and adhesive friction; (b) plastic deformation, associated with abrasive wear, friction ploughing, and/or cutting; (c) fracture, associated with fatigue wear and surface damage; (d) phase changes, associated with surface melting and recrystallization of metals; (e) chemical reactions, associated with chemical and oxidation wear; (f) diffusion, associated with gradient induced migration of material; (g) mixing, which for tribology involves mixing of third body material entrained between surfaces. All these dissipative processes and their contribution to entropy generation make the analysis complex. Dai [28], however, presents a less complex form of entropy generation for a tribosystem merely considering heat conduction, thermo-diffusion, plastic deformation and chemical reaction. The entropy generation for a tribosystem can be expressed in terms of thermodynamic forces and fluxes as:

$$\sigma = X_i J_i = \mathbf{q} \cdot \nabla \left( \frac{1}{T} \right) + \frac{\sigma}{T} : \dot{\boldsymbol{\epsilon}}_P + \sum_j \frac{A_j}{T} v_j - \sum_k \mathbf{J}_k \cdot \nabla \left( \frac{\mu_k}{T} \right) \quad (29)$$

where  $\mathbf{q}$  is the vector of heat flux,  $\sigma$  is the stress tensor,  $\dot{\boldsymbol{\epsilon}}_P$  is the rate of plastic strain tensor,  $A_j$  is chemical affinity,  $v_j$  is velocity of chemical reaction,  $\mathbf{J}_k$  is the vector of diffusion flux and  $\mu_k$  is the chemical potential of component  $k$ . Here the entropies of the dissipative processes, acting as influence functions, provide the influence of specific dissipative processes on the total friction and wear. Therefore, invoking Equations (28) and (29) and knowing the fact that  $\dot{m}_e$  is the rate of worn out material, it is possible to quantify wear damage via measuring entropy generation. It is however, easier to use Equation (28) if the process is at steady-state condition. This has been shown by Doelling *et al.* [18].

### 3.6. Radiation Damage

According to Was [86] radiation damage is defined as the transfer of energy from an incident projectile to a solid and resulting distribution of target atoms after completion of the event. For example, radiation damage occurs in crystal irradiation by neutrons created from nuclear fission. Because the neutrons collide with the nuclei of incident atoms, kinetic energy is transferred to knocking the incident nuclei out of their lattice sites. As a result, there will be a number of vacant lattice sites and an equal number of displaced atoms known as radiation damage [96].

Radiation damage is a major concern in, for example, reactor pressure vessels (RPV). Neutron irradiation is the cause of RPV embrittlement. Concerns associated with radiation damage of nuclear materials will significantly influence their operational lifetime. Better understanding of the underlying causes of radiation damage will provide better estimates of materials-operating margins [97].

We present the thermodynamic assessment of radiation-induced damage developed by Valanis [98]. Valanis adopted the concept of internal variables to show that neutron irradiation can be explained physically and can be evaluated quantitatively by means of irreversible thermodynamics. An input of radiation energy in a material microstructure induces forces  $A_r$ , which are called internal forces and are associated with deformation  $v_r$ . Therefore, if  $\dot{q}$  is the rate of energy input by radiation, it can be written as [98]:

$$\dot{q} = \dot{q}_t + \sum_r A_r \dot{v}_r \quad (30)$$

where  $\dot{q}_t$  is the energy input by thermal radiation. The second term on the right-hand side of Equation (30) represents the energy input by radiation due to internal forces causing microstructural changes. Considering this term merely, the entropy generation due to radiation damage can be written as:

$$\sigma = X_i J_i = \sum_r \frac{A_r}{T} \dot{v}_r. \quad (31)$$

Accordingly, the internal microstructure motion due to radiation constructs the thermodynamic flux  $J = \dot{v}_r$  driven by the internal forces as the thermodynamic force  $X = A_r/T$ . The thermodynamic force in radiation damage is associated with the neutron flux density, and thermodynamic flux depends on the average velocity of the atoms after neutron collision. To show such dependencies, Valanis [98] presents the following relationship for the average force,  $F$ , in the case of unidirectional collision of neutrons with stationary atoms:

$$F = \frac{2v_0 P m M}{N(m + M)} A_r \quad (32)$$

where  $v_0$  is the average neutron velocity,  $P$  is the probability of collision per neutron per volume,  $m$  is the mass of neutron,  $M$  is the mass of the nucleus of the target material,  $N$  is the number of the target atoms per unit volume, and  $A_r$  is the neutron flux density (or the thermodynamic force as mentioned above). The entropy generation per unit volume for this unidirectional case can then be written as:

$$\sigma = \frac{A_r}{T} \left( \frac{2v_0 P m M}{N(m + M)} V \right) \quad (33)$$

where  $V$  is the average velocity of an initially stationary atom after the collision [98]. Therefore, the thermodynamic flux is  $J = \dot{v}_r = \frac{2v_0 P m M}{N(m + M)} V$ . It is obvious from Equation (33) that the entropy generation in neutron radiation associates neutron flux density to the structural damage caused by neutron collision, and thus is a measure of radiation damage.

### 3.7. Creep Damage

Creep is defined as progressive accumulation of plastic strain in a specimen under stress at elevated temperature over a period of time [99]. A typical creep test involves subjecting a specimen to a constant load or stress while maintaining a constant temperature. Strain (or deformation) is then measured and plotted as a function of elapsed time [100]. Creep failure occurs when the accumulated creep strain results in a deformation of the system or component part that exceeds the design limits. It is a predominant failure mechanism of all types of material in engineering applications with high operating temperature, such as steam turbines in power plants, jet and rocket engines, and nuclear reactors.

According to Lemaitre and Desmorat [101] “[f]rom a physical point of view, creep damage in metals is essentially the nucleation and growth of intergranular microcracks up to crystals triple points where the coalescence of microcracks induce a mesocrack.” Kachanov (1958) was perhaps the first one to introduce the continuous damage variable as a measure of nucleation, growth, and coalescence of defects, such as microvoids and microcracks, for modeling creep failure. After Kachanov, other

researchers [6,102–105] have also used the concept of the damage variable to model creep damage. In creep damage, however, treating material as a continuum medium, and also describing damage via a single damage variable, may overshadow the influence of microstructural features (e.g., grain size, grain orientation, and slip systems) on the damage evolution [105]. In fact, creep damage involves several sub-mechanisms such as vacancy diffusion and lattice site generation and annihilation, while the continuum Equations appear to describe only one, the void nucleation and growth [105]. Therefore, an effective creep damage model must to be physically inspired and include contributions of all sub-mechanisms on overall damage.

Accordingly, thermodynamic based approaches have been taken [106,107] which account for entropy generation due to each sub-mechanism. For example, Mishin *et al.* [107] developed an irreversible thermodynamics framework to assess creep deformation in crystalline solids by mechanisms that involve vacancy diffusion, lattice site generation and annihilation. They presented an expression for entropy generation in terms of thermodynamic forces and fluxes relevant to sub-mechanisms active in creep damage. The entropy generation is then used to serve as the starting point for the formulation of phenomenological relations between forces and fluxes. Without going through the derivation here, we merely present the final expression for the entropy generation developed by Mishin *et al.* [107] for the creep process:

$$\begin{aligned} \sigma = & \frac{1}{T} \mathbf{q} \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \sum_{i=1}^n \nabla (M_i + \psi_i) \cdot \mathbf{J}_i - \frac{1}{T} \sum_{j=1}^N \Phi_j \frac{d^l \varphi_j}{dt} \\ & + \frac{1}{T} (\boldsymbol{\sigma} - \tilde{\boldsymbol{\sigma}} - \mathbf{A}^*) : \nabla \mathbf{v}_l + \frac{1}{T} (\tilde{\boldsymbol{\sigma}} - \omega \mathbf{I}) : \mathbf{R} \end{aligned} \quad (34)$$

where  $\mathbf{q}$  is the heat flux vector;  $M_i$  is the chemical potential of species  $i$ ;  $\psi_i$  are species-specific potential functions;  $\mathbf{J}_i = n_i (\mathbf{v}_i - \mathbf{v}_l)$  is the diffusion flux of species  $i$  relative to the lattice with  $\mathbf{v}_i$  as its observed velocity relative to the laboratory and  $n_i$  is the number density of each material species;  $\mathbf{v}_l$  is the lattice velocity; and  $\varphi_j$  and  $\Phi_j$  represent the phase fields and diffusion potentials, respectively. Phase fields describe the microstructure evolution during creep which gives rise to redistribution of vacancy sinks and sources in the material.  $\boldsymbol{\sigma}$  is the stress tensor per unit volume of material.  $\tilde{\boldsymbol{\sigma}}$  and  $\omega$  are the equilibrium Cauchy stress in a uniform lattice and the equilibrium hydrostatic pressure, respectively.  $\mathbf{I}$  is the unit tensor and  $\mathbf{R}$  is the creep deformation rate. Each term in Equation (34) describes the entropy generation due to: (1) heat conduction, (2) diffusion driven by gradients of the chemical potentials  $M_i$ , (3) evolution of the phase fields  $\varphi_j$ , (4) viscous dissipation by conversion of the strain rate to heat (e.g., generation of phonons), and (5) annihilation of lattice sites [107]. Each term can be realized as the product of a driving force(s) and a conjugate thermodynamic flux(es). Equation (42) suggests that the creep deformation rate  $\mathbf{R}$  not only depends on its conjugate force,  $(\tilde{\boldsymbol{\sigma}} - \omega \mathbf{I})/T$ , but also on various sub-mechanisms that are possibly active during the course of creep. This dependency is realized through entropy generation.

**Table 1.** A summary of thermodynamic variables associated with damage mechanisms

Primary mechanism	Thermodynamic force, $X$	Thermodynamic flow, $J$	Examples of materials damage process
Heat conduction	Temperature gradient, $\nabla(1/T)$	Heat flux, $\mathbf{q}$	Fatigue, creep, wear
Plastic deformation of solids	Stress, $\sigma/T$	Plastic strain, $\dot{\epsilon}_p$	Fatigue, creep, wear
Chemical reaction	Reaction affinity, $A_k/T$	Reaction rate, $v_k$	Corrosion, wear
Mass diffusion	Chemical potential, $-\nabla(\mu_k/T)$	Diffusion flux, $J_k$	Wear, creep
Electrochemical reaction	Electrochemical potential, $\tilde{A}/T$	Current density, $i_{corr}/z$	Corrosion
Irradiation	Particle flux density, $A_r/T$	Velocity of target atoms after collision, $\dot{v}_r$	Irradiation damage
Annihilation of lattice sites	Creep driving force $(\tilde{\sigma} - \omega\mathbf{I})/T$	Creep deformation rate, $R$	Creep

Table 1 shows a summary of the thermodynamic forces and fluxes for some of the irreversible processes discussed above.

### 3.8. Synergistic Effect

In general,  $n$  degradation processes may be simultaneously involved so that thermodynamic fluxes  $J_i$  are functions of their conjugate forces  $X_i$  as well as all other driving forces  $X_j$  ( $j \neq i$ ) and temperature  $T$  [108]. That is:

$$J_i = J_i(X_1, \dots, X_n, T); \quad (j = 1, 2, \dots, n) \quad (35)$$

We assume, for simplicity, that thermodynamic flux is only a function of driving forces [59]. It is known empirically that for a large class of irreversible phenomena and under a wide range of experimental conditions, the irreversible fluxes are a linear function of the thermodynamic forces [62]. Therefore, for linear processes:

$$J_i = L_{ik} X_k; \quad (i, k = 1, 2, \dots, n) \quad (36)$$

The quantities  $L_{ik}$  are the so-called *phenomenological coefficients*, and Equation (36) is referred to as the *phenomenological Equation*. If, for instance  $n = 2$ , coefficient  $L_{11}$  determines the effect of force  $X_1$  on its conjugate flux  $J_1$ , and the coefficient  $L_{12}$  determines the effect of force  $X_2$  as it drives its cross flux  $J_1$ . This is known as the *cross coupling effect* or synergistic effect. As discussed earlier, the existence of cross coupling makes the system under study complex. For linear processes, the entropy generation can be written as:

$$\sigma = L_{ik} X_i X_k; \quad (i, k = 1, \dots, n) \quad (37)$$

Note that the entropy generation in Equation (8) takes the form of a quadratic function for linear systems. For the linear phenomena, the well-established *Onsager reciprocal relations* between phenomenological coefficients are  $L_{ij} = L_{ji} \forall i \neq j$  [7]. Let us assume a complex system including fatigue and corrosion interaction. In corrosion-fatigue, not only does the stress cause the flow of dislocation, but also the anodic current present at the electrode surface can increase the mobility of dislocation and reduce the resistance against plastic deformation [10]. Summing the contributions of the mechanical and electrochemical processes, we can write the total entropy generation for combined effect of plastic deformation and dissolution as:

$$T\sigma = \sigma : \dot{\epsilon}_p + \frac{\tilde{A}i_{corr}}{z} \quad (38)$$

Therefore, we can write the following system of phenomenological Equations to take the cross effects of two processes into consideration:

$$\begin{aligned} \dot{\epsilon}_p &= L_{11}\sigma + L_{12}\tilde{A} \\ \frac{i_{corr}}{z} &= L_{21}\sigma + L_{22}\tilde{A} \end{aligned} \quad (39)$$

It is to be mentioned that in Equation (39) the system is assumed to be isothermal and plastic strain rate is linearly correlated with stress. The term  $L_{12}\tilde{A}$  represents the increment in the rate of plastic deformation induced by electrochemical current density, and the term  $L_{21}\sigma$  represents the increment in corrosion current density induced by plastic deformation. The above analysis indicates that the rate of corrosion can be enhanced in the presence of cyclic plastic deformation and *vice versa*: fatigue damage can be enhanced if in a corrosive environment.

### 3.9. Structural Reliability and Health Assessment

Despite the significant advances in data driven prognostics approaches and Physics-of-Failure (PoF) methods that underlie reliability prediction and structural integrity assessment, a significant gap exists between engineering approaches and science to capture damage evolution suitable for structural health assessment, early failure prediction, accelerated failure testing, and methodologies for prediction of remaining useful life. In fact, the data driven methods such as neural networks [109], decision tree classifiers [110] and Bayesian techniques [111] do not capture the difference between failure modes and mechanisms, although they can obtain the complex relationship and degradation trend in the data without the need for the particular product characteristics such as degradation mechanism or material properties. The PoF models are more rigorous in terms of employing the specific knowledge of products, such as failure mechanism, material properties, loading profile and geometry. However, such empirical methods are limited to simple failure mechanisms and are hard to model when multiple competing and common cause failure mechanisms are involved. As an emerging field, the thermodynamics of structural reliability and health assessment in recent years saw a boost in research and development [112–117]. Imanian and Modarres [114] developed an entropy-based prognostics method using particle filter to update the states of the model, reduce uncertainties and predict the remaining useful life probability distribution function. They used Mahalanobis Distance (MD) approach as a diagnostic threshold that triggers their remaining useful life prediction. Anomalies were identified when the MD threshold of the test entropy data crosses the anomaly detection threshold. Upon detection of anomaly, particle filter algorithm was used to predict probability distribution function of the remaining useful life of their test specimens. Their entropy-based prediction of remaining useful life provides satisfactory results. Entropy approach includes all degrading mechanisms when multiple competing and common cause failure mechanisms are involved, therefore, using it as a damage parameter for diagnosis and prognostics is more favorable in comparison with the PoF models and data driven models which merely rely on the most predominant failure mechanisms and the statistical analysis, respectively. While the thermodynamic method proved to provide a sound

physical-based foundation relevant for reliability analysis and structural health assessment, its practical advantages remain to be explored.

#### 4. Conclusions

This paper presents a thermodynamic framework for assessment of materials damage using entropy generation as a measure of damage. It was suggested that a unified measure of damage can be defined based on entropy generation. Examples of some degradation processes were discussed and damage was identified in terms of thermodynamic forces and fluxes. It was shown that the entropic method can provide both fundamental understanding of degradation mechanisms and quantification of damage. Assumptions and constraints such as the local-equilibrium hypothesis and those associated with MEPP were discussed. It was also suggested that entropic concept has been theoretically well developed for fatigue damage and wear damage mechanisms with considerable experimental validation and that further experimental works are required to extend the concept for other damage mechanisms. The approach presented in this paper offers a new and promising area of research in the fields of materials damage modeling, reliability engineering and structural health assessment. Although entropic method, in the past, has rarely been used by practical engineers, this method has a significant potential of practical application in the fields of damage analysis, engineering reliability and structural health assessment. Recent entropic works and advances in two research communities: materials damage assessment and reliability engineering offer new and exciting research opportunities in these fields for years to come.

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#### Author Contributions

Both authors contributed equally to the development of this work. Both authors have read and approved the final manuscript.

#### Conflicts of Interest

The authors declare no conflict of interest.

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