Beyond Miner's Rule
Free Energy Damage Equivalence (Part II)

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SUMMARY & CONCLUSIONS

In part I of the paper published [1] last year, we extend the concept of damage originally developed empirically by Miner, using the concept of thermodynamic work and free energy. We first explain the equivalency of free energy to damage where a products free energy is the amount of useful work that a product can deliver. Knowledge of this provides useful lifetime estimates. We develop ways to measure the free energy in products to help assess its lifetime. The main approach is to use what we call a product's "Ultimate" work energy.

In this paper, we explore practical applications in the area of fatigue and battery cycle life. Often when a new approach comes along, it is not easy to fully appreciate its applicability. Therefore, in this paper we will provide these new added examples applied to Aluminum fatigue and battery cycle life; These somewhat different areas 1) fatigue of metals and 2) an energy device, allows one to gain deeper insight into the free energy approach to determining a products useful life time. This will exemplify the efficiency of the "Ultimate" work energy damage equivalence approach for doing common but challenging problems. Example illustrate that tools like the S-N curve while obviously illustrative, are not necessary and perhaps not the best way to characterize materials, as well this approach is anticipated to reduce experimental measurement time.

A deeper understanding of the free energy damage equivalency approach entails knowledge of a specific work path to a particular problem. Once applicability is understood, the tool should be helpful for numerous areas in physics of failure applications.

1. INTRODUCTION

As a summary of the first paper we started with Miner's Rule [2] written by Miner in terms of a ratio for n_i cycles performed to N_i cycles to failure per each i^{th} stress level as

$$Damage = \frac{n_1}{N_1} + \frac{n_2}{N_2} + \ldots + \frac{n_k}{N_k} = \sum_{i=1}^{K} \frac{n_i}{N_i} \qquad (1)$$

We noted the uniqueness of this rule as it presented back in 1945 the concept of quantifying damage whether it is cumulative or otherwise. We then described the energy approach [3]. The energy approach goes beyond Miner's rule for it is more general and exact. In the evolution of the energy approach we measure damage in thermodynamic work terms W [3] as

$$Damage = \frac{\sum W_{actual}(t)}{W_{actual-failure}} \qquad (2)$$

Thus, we have a physics of failure law for damage whose origin came from Miner's formulation.

We pointed out that one of the key issues is the value of the work to failure in the denominator? If we know this we are in a good position to assess damage.

2. FREE ENERGY AND DAMAGE

We noted that in thermodynamics, a materials free energy provides an assessment of the amount of useful work that a product can perform. Therefore, products lifetimes can be assessed using this approach and reduced test times are anticipated because once you know the free energy at one stress level, it is the same for all stress levels. This is clearly demonstrated in our examples here.

In Section 2-5 we will for convenience, summarize the concept of free energy-damage approach developed in the first paper for the reader. However, we strongly recommend that the reader obtain the original paper.

In the original paper we noted that the *work that can be done on or by the system is bounded by the system's free energy [2]*

$$Work \leq \Delta \text{ Free Energy Change of the system} \qquad (3)$$

This is the key concept that is developed.

3. FREE ENERGY DAMAGE EQUIVALENCE

From Equation 3, we propose that a materials Ultimate Work Energy (W_{UE}) for a given failure mode or mechanism is the most measurable and useful property to assess a materials free energy

- $(\Delta\text{Free Energy})_j^{th} \geq (\text{Maximum Ultimate Work Energy})_j^{th} = (\text{Maximum Damage Amount})_k^{th}$

(4)

where 'j' is for the j^{th} type failure mode/mechanism of failure. Again once we know the free energy for the work path of interest, we can estimate the products useful work and life.

As damage increase, the free energy decreases and so does the available useful work. If the system's initial free energy is denoted by F_i (before aging) and the final free energy is denoted by F_f (after aging), then $F_f < F_i$ and

$$F_i - F_f = (\Delta Free\,Energy)_{Max-damage} = W_{failure}(UE) \quad (5)$$

This is the free energy damage equivalence. Damage equivalency as originally developed by Miner, is a unitless quantity and from Equation 5 is

$$Damage = \frac{\Delta Free\ \ Energy}{(\Delta Free\ \ Energy)_{Max-damage}} = \frac{\Delta Free\ \ Energy}{W_{failure}(UE)},$$
$$and\ D = 1,\ when\ \ \Delta Free\ Energy = W_{failure}(UE) \quad (6)$$

When cumulative damage reaches the value D=1, failure occurs.

4. ULTIMATE WORK ENERGY

In the original paper we denoted $W(UE)_{0+}$ as a measurement of the ultimate work energy

$$W(UE)_{0+} \approx W(UE) \quad (7)$$

The concept is to measure the ultimate work energy in a short time (i.e., 0+) so that it is reasonably accurate and representative of the actual ultimate work and product life.

Once we know the W(UE) for a particular failure mode, then energy can be subtracted when work is accomplished as damage accumulates.

If interim work is denoted by *Wi*, then the work remaining, *Wr*, in a product is

$$Wr=W(UE)-Wi \quad (8)$$

5. FATIGUE AND ULTIMATE WORK ENERGY

In this paper we will focus on fatigue examples. Here we provide a quick review of fatigue concepts from our first paper. In our first example, we will make use of an expression for fatigue cyclic work, we look at plastic strain (ε) caused by a sinusoidal vibration level G stress (σ) in the material. A common model for the strain in this case is [3]

$$\varepsilon = \beta_o n^p G^j \quad (9)$$

The cyclic work is found as [1,3]

$$w = \oint_{\Delta L} \sigma\, d\varepsilon = \oint_{\Delta L} G \frac{d\varepsilon}{dn} dn = A G^{j+1} n^P = A G^Y n^P \quad (10)$$

where Y=j+1. Similar to the above arguments, to assess the damage we need to have some knowledge of the critical damage at a vibration stress level. Let's assume this occurs at N_1 cycles at stress level G_1. Then the thermodynamic damage ratio at any other stress G_2 level at n_2 cycle is [1, 3]

$$D_{vib} = Vibration\ Damage = \frac{w}{W_F} = \left(\frac{n_2}{N_1}\right)^P \left(\frac{G_2}{G_1}\right)^Y \quad (11)$$

If damage is represented by D_{vib}=1, $n_2 = N_2$, and failure occurs. We note the time acceleration factor is obtain in terms of cycles (N=f T, f is the frequency is considered constant, T is the time) as [3]

$$AF_D = \frac{T_1}{T_2} = \left(\frac{N_1}{N_2}\right) = \left(\frac{G_2}{G_1}\right)^b \quad (12)$$

where b=Y/P. AF_D is commonly used relationship for cyclic compression where we assumed the frequencies f_1=f_2.

It is helpful to write the linear form for cycles to failure, for a particular stress. This is deduced to within a constant from the above equation (12)

$$N_1 = A(G_1)^{-b} \equiv A(G_{rms-1})^{-b} \quad (13)$$

where $A = N_2 / G_2^{-b}$ treated as a constant. This is essentially the relation that holds for what is called the S-N curves. Note that if we write the cyclic equation with $G \propto S$ where S is the stress, we have

$$N_1 = C\,S_1^{-b} \quad \text{or} \quad S_1 = K\,N_1^{-B} \quad (14)$$

where B=1/b and C is the proportionality constant when going from G to S and K is a constant. The relationship is generally used to analyze S-N data, this is formally known as Basquin's equation which is used in the area of high cyclic fatigue.

6. EXAMPLE : ULTIMATE WORK ENERGY - STAINLESS STEEL FATIGUE LIFE

We are now in a position to look at an example. To use this approach for fatigue, first we need to understand that fatigue is dominated by tensile force rather than compressive force. That is, most of the damage in fatigue is due to tensile (rather than compressive) work. This helps us to identify the material's key property that we would need to know. Using the ultimate energy approach we will solve the following problem without an S-N curve and make comparisons:

- T6 Aluminum 6061 alloy breaks apart at 10^3 cycles of work at a tensile stress of 310 MPa with a strain change of ~17%. A good indication of its ultimate work energy. Knowing the $W(UE)_+$, find a rough estimated of the fatigue cycle life at 175 MPa and compare it to SN curve prediction. Use Eq. 11 for the thermodynamic work (assume Y=8).
- Show that Miner's assumption in this case still seems reasonable. What is it about the S-N curve that appears to indicate that Miners assumption will eventually be off? Find P to fit the S-N curve in Figure 1.
- Provide a check that the ultimate work energy is the same at stress level 310 MPa as it is at 175 MPa.

In our theory, we might be tempted to use N=1 cycle as the point to assess the free energy. However, the further we are away from N=1, the more accurate the free energy estimate is likely to be for S-N curve ultimate energy so 1000 cycles may be an excellent point to estimate the ultimate energy. The S-N curve for Aluminum is shown below.

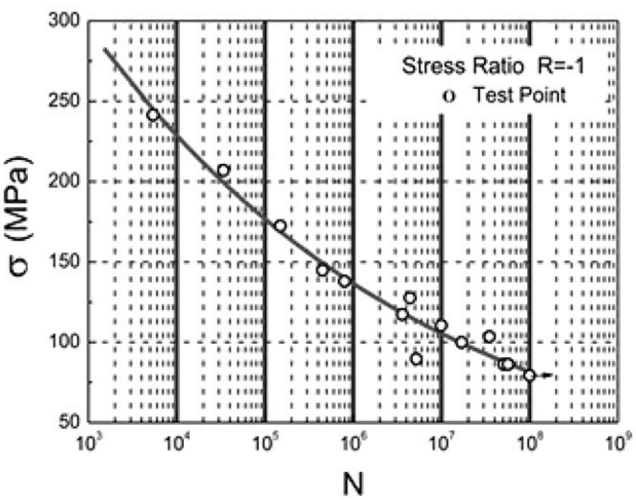

Figure 1 S-N Curve of 6061-T6 aluminum alloy [6]

Summarizing the problem statement

- Let S_2=310 Mpa, N2=1000, S_1=175 Mpa, what is N1 and P?

Then we must have for work to failure $W_2=W_1$ such that D=1 in Eq. 11 so we write

$$D=\left(\frac{W_2}{W_1}\right)\equiv\left(\frac{S_2}{S_1}\right)^8\left(\frac{N_2}{N_1}\right)^P=1 \qquad (15)$$

Here we have substituted S=G in Eq. 11 and taken the work ratio. Note this physics of failure approach is strictly due to the ultimate strength free energy approach with the Miner's assumption of P=1, so that from Eq. 10

$$W(N,S)=NW(S)=As^Y N \qquad (16)$$

One should also realize that the physics of failure equation above is for a specific work path due to tensile loading of the aluminum shaft. Other alternate loading may require modification. For example, shaft smoothness, shear issues in the work path etc. Therefore Eq. 15 and 16 are for a specific work path and is key in applying this theory. Solving for N_1 Eq. 15 gives us

$$N_1\equiv\left[\left(\frac{310}{175}\right)^8 1000\right]=9.7E4\approx 1E5 \qquad (17)$$

We can make a comparison to the S-N curve and we find excellent accuracy of N=1E5 cycles at 175 MPa. Here we did not need the S-N curve; we needed knowledge only of the ultimate work energy and the physic of failure equation for the work path.

Note that if we did intermediate work of type W2, and W3 we can actually subtract off the work to find the remaining work then proceed to find N_1 as above,

$$W(Remaining)=W(UE)-W3-W2 \qquad (18)$$

Then the predicted cycles to failure at any stress level is

$$N=W(Remaining)/AS^Y \qquad (19)$$

Recall that S=310 MPa, N=1000 cycles, and W(UE) value must actually be found in joules of work that is not reported here to determine the W(UE).

Note that S-N curve shows a non straight line on the semi log plot. This indicates that N is showing some non linear effect so Miner's rule may eventually be off (i.e. P≇1) somewhat. An estimate fitting the curve with Y=8 is P=0.997. So Miner's assumption is fairly reliable.

Lastly check Eq. 15 showing that the free energy is the same at the two stress levels of 175 and 310 MPa where

$$D=\left(\frac{W_2}{W_1}\right)\equiv\left(\frac{S_2}{S_1}\right)^8\left(\frac{N_2}{N_1}\right)=\left(\frac{310}{175}\right)^8\left(\frac{1000}{9.7E4}\right)=0.996 \quad (20)$$

This is very close to 1, as required. This simply also reminds us that the free energy can be found at any stress level. Obviously a high stress level reduces experimental test time.

EXAMPLE: ULTIMATE WORK ENERGY FOR SECONDARY BATTERIES

We have already provided an example for primary (non rechargeable) batteries [1] in part 1 of the original paper. Here we will apply this method to secondary (rechargeable) batteries.

We offer two Models to aid battery manufactures in cycle life predictions.

METHOD 1: MINER'S RULE MODELS

Although metal fatigue quite often uses Miner's rule in assessing cycle life, battery manufacturers are either not familiar with this method or understand its applicability to battery cycle life as has been previously described [5].

In terms of Miner rule approximation we have from Equation 2

$$Damage=\frac{\sum_j w_{actual}(t)_j}{W_{actual-failure}}=\frac{\sum_j n_j w_j}{N_j w_j}=\frac{\sum_j n_j}{N_j} \quad (21)$$

Battery manufacturers find the N cycles to failure as a function of Depth of Discharge (DoD). For example, if a battery has 10% of it charge remaining, its DoD is 90%. They would then recharge it and repeat n cycles, after a certain number of cycles N, the battery is unable to recharge. Now we deduce that this work to failure is the same amount for any cyclic Depth of Discharge (DoD) size and approximately equal to the ultimate energy, that is

$$W(UE)=N_1w_1=N_2w_2=N_3w_3...=N_jw_j \quad (22)$$

This will be verified in Method 2 as was checked for metal fatigue in Eq. 20. During a cycle in which there is both charging and discharging of the chemical cell, the work w_j for a cycle of type C_j (DoD amount) can be measured

$$w_j=\oint_{C_j} v\,dq=\oint_{C_j} v\frac{dq}{dt}dt\approx vit_{C_j} \quad (23)$$

where v is the chemical cells voltage, i is the current and t is the time. This presents actually two useful equations to determine damage. The first being

$$Damage=\frac{\sum_j n_j w_j}{N_k w_k} \quad ,W(UE)=N_1w_1=N_2w_2... \quad (24)$$

Here we see we can measure the Ultimate work energy easily at any reasonable cyclic size, say DoD=90% and have knowledge of the denominator. Then at any other cyclic size, predict with knowledge of w_j for say 20% DoD what the number of cycles left will be. For example, if we measure at a DoD=90% that $W(UE)=N_{90\%}w_{90\%}=10{,}000$ Joules and at a DoD=20% we measure for a cycle $w_{20\%}=10$ joules, we anticipate $N_{20\%}=1000$ yielding *Damage=1*.

Alternately, we have the option of using Miner's rule as

$$Damage=\frac{\sum_j n_j}{N_j} \quad (25)$$

In Eq. 25, we are not making use of *W(UE)* but are taking advantage of the simplicity of Miner's rule in applying it to batteries similar to metal fatigue. However, here we must determine N_j for any cyclic *DoD* size of interest.

METHOD 2: MODELING THE ULTIMATE WORK ENERGY APPROACH

Modeling the battery work path using a physics of failure type approach has more predictive capability and provides insight into battery life. In metal fatigue we focused on the stress (s) strain (e) relationship $dw=\sigma\, de$. However, for batteries the conjugate stress-strain analogy [3] $w= v\, dq$ is a bit more challenging as batteries are thermally activated as well battery manufacturer's present life data analysis in terms of DoD and cycles.

The thermally activated ultimate free energy cycle life model is found in the Appendix and is given by

$$W(UE)=\frac{1}{f_c}N_oV_o\,i\,e^{DoD} \quad (26)$$

Here N_o is the cycles to failure (see Eq. A-3) at the given DoD rate, i is the cycle current, and V_o is the voltage (see Eq. A-4). Figure 2 provides typical DoD battery cycle life. Here it is for Ni-Fe secondary battery cycle life [6]. We fitted the data in Ref. 8 to two models. The first is a simple power law that one might be tempted to use without any physics applied, the second is based on the thermally activated model found in the Appendix. We see the Appendix model is very accurate fit with R^2=0.9985 compared to the non based physics of failure model as is displayed in the Figure 2 curve fit. The activation energy exponent is found in the fit of 0.031 taken as unitless here (see A-5)

$$N=849159\ DoD^{1.456} \quad R^2=0.9678 \qquad (27)$$

$$N=15428\ Exp(-0.031DoD) \quad R^2=0.9985 \qquad (28)$$

Note that although the value 0.031 was found using extensive data in Figure 2, it could have been obtained either from assessing the free energy or found with just a few points say at 80 and 90% DoD levels to reduce test time.

In Figure 2, the exponential curve one can utilize Eq. 28 as $N=N_o exp(-b\ DoD)$ which is supported in the Appendix with Equations A-3, A-5, and A-6.

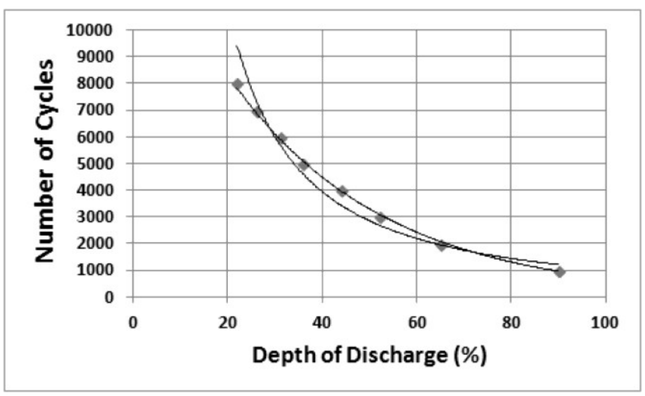

Figure 2 Typical cycle life versus DoD (this curve for Ni-Fe battery life cycle) [6]

Let's apply the ultimate energy approach to the problem. We simplify the model for instructive purpose as

$$W_i= a\ N_i\ Exp\ (b\ DoD_i), \quad b=+0.031 \qquad (29)$$

Where 'a' and 'b' are model constant with physical relevance provided in Equation 26, *N* is the cycles to failure at the *DoD* level. Similar to the metal fatigue case, we will only need b for the analysis for the following example:

- For Ni-Fe Battery cycle life, it is found that it fails at N=1000 cycles for 90% DoD. This is a good indication of the batteries ultimate work energy capability. Knowing the $W(UE)_+$ capability, find a rough estimated of the fatigue cycle life at 26% DoD and compare it to Battery cycle life curve prediction. Use Eq. 29 for the thermodynamic work (assume b=0.031).
- Check that the ultimate work strength is the same at 90% DoD as it is for 26% DoD.

Summarizing the problem statement

- Let DoD_2=90%, N2=1000, S_1=26%, what is N1?

Then we must have for work to failure $W_2=W_1$ such that D=1

$$D=\left(\frac{W_2}{W_1}\right)=1 \qquad (30)$$

Plugging Eq. 29 into the above and solving for N_1

$$N_1 \equiv \left[\left(\frac{Exp(0.031x90}{Exp(0.031x26}\right)1000\right] = 7272 \qquad (31)$$

We can make a comparison to the DoD curve and we find excellent accuracy of N=7272 cycles at 26%. Note we did not need the curve; we needed knowledge only of the ultimate work energy and the physic of failure equation for the work path and the thermal activation energy value of 0.031.

Lastly check Eq. 30 showing that the ultimate work energy is the same at the two stress levels at 26% and 90% DoD we write

$$D=\left(\frac{W_2}{W_1}\right)=\frac{7272\,Exp(0.031x26)}{1000\,Exp(0.031x90)}=1.0000316 \qquad (32)$$

as required. This verifies the ultimate work energy consistency throughout the DoD life cycle and provides confidence in the physics of failure expression in Eq. 26.

APPENDIX A: BATTERY CYCLE LIFE MODEL

The work for charge-discharge cycling similar to Eq. 23 is [3, 5]

$$w=\oint_{\Delta L} v\ dq=\oint_{\Delta L} v\frac{dq}{dt}dt=v\ i\,t_c \qquad (A\text{-}1)$$

t_c is the cyclic time at the DoD of interest, *v* is the work stress voltage, *i* is the cyclic current. We introduce *n* cycles as charge-discharge time can be written with the aid of a frequency as

$$t_c=n/f_c \qquad (A\text{-}2)$$

where n is the work cycles at the DoD of interest, f is the frequency of cycles. However, since batteries are thermally activate the number of cycles to failure is also dependent on battery temperature T so that [3, 5] cycles to failure will be effected by temperature. We model this using an Arrhenius expression and now switch to failure cycles N (i.e., n cycles of work compared to N cycles to failure) as

$$N(T) = N_o e^{-\frac{\phi}{K_B T}} \quad \text{(A-3)}$$

Here ϕ is the thermal activation energy for cycle life and K_B is the well known Boltzmann's constant. The damage failure voltage must also be thermally activated dependent on temperature and we model it similarly as

$$V(T) = V_o e^{-\frac{vq}{K_B T}} \quad \text{(A-4)}$$

We make the substitution that

$$DoD(T) = \frac{-vq + \phi}{K_B T} \quad \text{(A-5)}$$

We see that $vq+\phi$ is formally the activation free energy not to be confused with the free energy.

Equation A-2, A-3, A-4 and A-5 allow us to write the ultimate work energy as

$$W(UE) = \frac{1}{f_c} N_o V_o \, i \, e^{DoD} \quad \text{(A-6)}$$

Note we have at this point substituted failure values N, so W is the ultimate work energy. The model indicates the ultimate work energy capability goes as DoD and N which makes sense. That is, we anticipate as DoD increase, N will decrease and W will stay the same (see Eq. 32 to clarify).

On a side note, for the purist, the thermodynamic free energy often denoted by symbol F (Eq. 3) is actually given by

$$dF=-SdT+Vdq \quad \text{(A-7)}$$

where S is the entropy, T is the temperature, V is the electromotive force (voltage), and q is the charge. If we hold the temperature constant this simplifies our free energy measurement task, where the work is bounded by the free energy as discussed in Eq. 3 such that for

$$dT = 0, \qquad \delta w \le dF = Vdq \quad \text{(A-8)}$$

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