

Article

Thermodynamic Analysis of Resources Used in Manufacturing Processes

Timothy G. Gutowski, Matthew S. Branham, Jeffrey B. Dahmus,
Alissa J. Jones, Alexandre Thiriez, and Dusan P. Sekulic

Environ. Sci. Technol., **2009**, 43 (5), 1584-1590 • DOI: 10.1021/es8016655 • Publication Date (Web): 29 January 2009

Downloaded from <http://pubs.acs.org> on February 28, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Thermodynamic Analysis of Resources Used in Manufacturing Processes

TIMOTHY G. GUTOWSKI,*
MATTHEW S. BRANHAM,
JEFFREY B. DAHMUS, ALISSA J. JONES,
AND ALEXANDRE THIRIEZ

Department of Mechanical Engineering, Massachusetts
Institute of Technology, Cambridge, Massachusetts 02139

DUSAN P. SEKULIC

Department of Mechanical Engineering, University of
Kentucky, Lexington, Kentucky 40506

Received June 17, 2008. Revised manuscript received
October 8, 2008. Accepted December 2, 2008.

In this study we use a thermodynamic framework to characterize the material and energy resources used in manufacturing processes. The analysis and data span a wide range of processes from “conventional” processes such as machining, casting, and injection molding, to the so-called “advanced machining” processes such as electrical discharge machining and abrasive waterjet machining, and to the vapor-phase processes used in semiconductor and nanomaterials fabrication. In all, 20 processes are analyzed. The results show that the intensity of materials and energy used per unit of mass of material processed (measured either as specific energy or exergy) has increased by at least 6 orders of magnitude over the past several decades. The increase of material/energy intensity use has been primarily a consequence of the introduction of new manufacturing processes, rather than changes in traditional technologies. This phenomenon has been driven by the desire for precise small-scale devices and product features and enabled by stable and declining material and energy prices over this period. We illustrate the relevance of thermodynamics (including exergy analysis) for all processes in spite of the fact that long-lasting focus in manufacturing has been on product quality—not necessarily energy/material conversion efficiency. We promote the use of thermodynamics tools for analysis of manufacturing processes within the context of rapidly increasing relevance of sustainable human enterprises. We confirm that exergy analysis can be used to identify where resources are lost in these processes, which is the first step in proposing and/or redesigning new more efficient processes.

Introduction

The main purpose of manufacturing processes is to transform materials into useful products. In the course of these operations, energy resources are consumed and the usefulness of material resources is altered. Each of these effects can have significant consequences for the environment and for sustainability, particularly when the processes are prac-

ticed on a very large scale. Thermodynamics is well suited to analyze the magnitude of these effects as well as the efficiency of the transformations. The framework developed here is based upon exergy analysis (1–5). The data for this study draw upon previous work in the area of manufacturing process characterization, but also include numerous measurements and estimates we have conducted. In all, we analyze 20 different manufacturing processes often in many different instances for each process. The key process studies from the literature are by, for microelectronics, Murphy (6), Williams (7), Krishnan (8), Zhang and Dornfeld (9), and Boyd (10), for nanomaterials processing, Isaacs (11) and Khanna (12), and, for other manufacturing processes, Morow and Skerlos (13), Boustead (14, 15), Munoz and Sheng (16), and Mattis and Sheng (17). Our own works include those by Dahmus (18), Dalquist (19), Thiriez (20, 21), Baniszewski (22), Kurd (23), Cho (24), Kordonowy (25), Jones (26), Branham (27, 28), and Gutowski (29). In addition, several texts and overviews also provide useful process data (30–35), and researchers are addressing thermodynamic reference states and alternative metrics which could be used with the models presented here (36–38).

Thermodynamic Framework

Manufacturing can be modeled as a sequence of open thermodynamic processes as proposed by Gyftopoulos and Beretta for materials processing (1). Each stage in the process can have work and heat interactions, as well as material flows. The useful output, primarily in the form of material flows of products and byproduct, from a given stage can then be passed on to the next. Each step inevitably involves losses due to an inherent departure from reversible processes and hence generates entropy and a stream of waste materials and exergy losses (often misinterpreted as energy losses).

Figure 1 depicts a generalized model of a manufacturing system. The manufacturing subsystem (Ω_{MF}) receives work W and heat Q from an energy conversion subsystem (Ω_{ECMF}). The upstream input materials come from the materials processing subsystem (Ω_{MA}), which also has an energy conversion subsystem (Ω_{ECMA}). This network representation can be infinitely expanded to encompass ever more complex and detailed inputs and outputs.

At each stage, the subsystems interact with the environment (at some reference pressure p_0 , temperature T_0 , and chemical composition, which is given by mole fractions x_i , $i \in (1, n)$, of n chemical compounds, characterized by chemical potentials μ_i). The performance of these systems can then be described in thermodynamic terms by formulating mass, energy, and entropy balances. Beginning with the manufacturing system Ω_{MF} featuring the system's mass M_{MF} , energy E_{MF} , and entropy S_{MF} , we have three basic rate equations.

$$\text{mass balance: } \frac{dM_{MF}}{dt} = \left(\sum_{i=1} \dot{N}_{i,\text{in}} \bar{M}_i \right)_{MF} - \left(\sum_{i=1} \dot{N}_{i,\text{out}} \bar{M}_i \right)_{MF} \quad (1)$$

where \dot{N}_i is the number of moles of the i th component entering or leaving the system and \bar{M}_i is the molar mass of that component.

$$\text{energy balance: } \frac{dE_{MF}}{dt} = \sum_k \dot{Q}_{ECMF,k}^{MF-} - \dot{Q}_0^{MF-} + \dot{W}_{ECMF}^{MF-} + \dot{H}_{MF}^{\text{mat}} - \dot{H}_{MF}^{\text{prod}} - \dot{H}_{MF}^{\text{res}} \quad (2)$$

* Corresponding author phone: (617) 253-2034; fax: (617) 253-1556; e-mail: Gutowski@mit.edu.

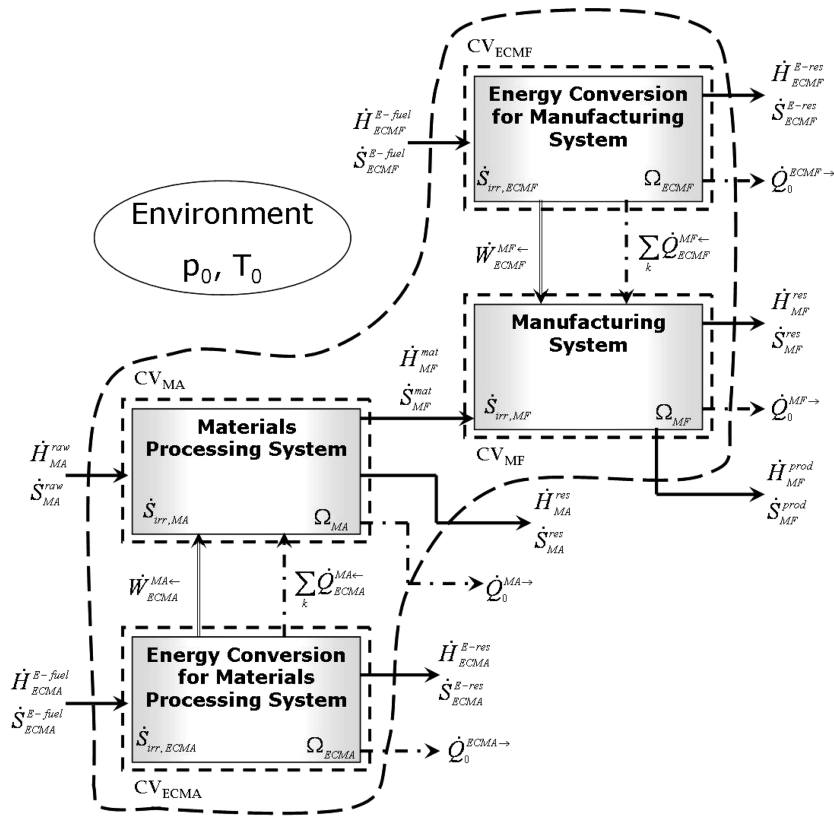


FIGURE 1. Diagram of a manufacturing system (27) (adapted from ref 1).

where $\dot{Q}_{ECMF,k}^{MF}$ and \dot{W}_{ECMF}^{MF} represent energy interactions between the manufacturing subsystem (Ω_{MF}) and its energy-supplying subsystem (Ω_{ECMF}). The \dot{H} terms signify the lumped sums of the enthalpy rates of all materials, products, and residue bulk flows into/out of the manufacturing system. Note that a heat interaction between Ω_{MF} and the environment, denoted by the subscript “o”, is assumed to be out of the system (a loss into the surroundings) at the local temperature T_0 .

$$\text{entropy balance: } \frac{dS_{MF}}{dt} = \sum_k \frac{\dot{Q}_{ECMF,k}^{MF-}}{T_k} - \frac{\dot{Q}_0^{MF-}}{T_0} + \dot{S}_{MF}^{mat} - \dot{S}_{MF}^{prod} - \dot{S}_{MF}^{res} + \dot{S}_{irr,MF} \quad (3)$$

where the \dot{Q}^{MF}/T terms represent the entropy flow accompanying the heat transfer rate exchanged between the subsystem Ω_{MF} and energy-supplying subsystem Ω_{ECMF} and environment, respectively, while \dot{S}_{MF} indicate the lumped sums of the entropy rates of all material flows. The term $\dot{S}_{irr,MF}$ represents the entropy production rate caused by irreversibilities generated within the manufacturing subsystem.

Assuming steady state and eliminating \dot{Q}_0 between eqs 2 and 3 yields an expression for the work rate requirement for the manufacturing process:

$$\dot{W}_{ECMF}^{MF-} = ((\dot{H}_{MF}^{prod} + \dot{H}_{MF}^{res}) - \dot{H}_{MF}^{mat}) - T_0((\dot{S}_{MF}^{prod} + \dot{S}_{MF}^{res}) - \dot{S}_{MF}^{mat}) - \sum_{k=0} \left(1 - \frac{T_0}{T_k}\right) \dot{Q}_{ECMF}^{MF-} + T_0 \dot{S}_{irr,MF} \quad (4)$$

The quantity $H - TS$ appears often in thermodynamic analysis and is referred to as the Gibbs free energy. In this case, a different quantity appears, $H - T_0S$. The difference between this and the same quantity evaluated at the reference state (denoted by the subscript “o”) is called flow exergy, $B = (H$

$- T_0S) - (H - T_0S)_o$. Exergy represents the maximum amount of work that could be extracted from a system as it is reversibly brought to equilibrium with a well-defined environmental reference state. In general, the bulk-flow terms in eq 4 may include contributions that account for both the physical and chemical exergies, hence $B = B^{ph} + B^{ch}$, as well as kinetic and potential exergy (not considered in this discussion); see refs 2–5.

The physical exergy is that portion of the exergy that can be extracted from a system by bringing a given state to the “restricted dead state” at a reference temperature and pressure (T_0, p_0). The chemical exergy contribution represents the additional available energy potential that can be extracted from the system at the restricted dead state by bringing the chemical potentials μ_i^* of a component $i \in (1, n)$ at that state (T_0, p_0) to equilibrium with its surroundings at the “ultimate dead state”, or just the “dead state” ($T_0, p_0, \mu_{i,0}$). In addition to requiring an equilibrium at the reference temperature and pressure, the definition of chemical exergies also requires an equilibrium at the reference state with respect to a specified chemical composition. This reference state is typically taken to be (by convention) representative of the compounds in the earth’s upper crust, atmosphere, and oceans. In this study, exergy values are calculated using the Szargut reference environment (5).

Substituting and writing explicit terms for the expressions for physical and chemical exergy allows us to write the work rate as

$$\dot{W}_{ECMF}^{MF-} = ((\dot{B}_{MF}^{prod,ph} + \dot{B}_{MF}^{res,ph}) - \dot{B}_{MF}^{mat,ph}) + \left(\sum_{i=1}^n b_{i,o}^{ch} \dot{N}_i\right)_{MF}^{prod} + \left(\sum_{i=1}^n b_{i,o}^{ch} \dot{N}_i\right)_{MF}^{res} - \left(\sum_{i=1}^n b_i^{ch} \dot{N}_i\right)_{MF}^{mat} - \sum_{k=0} \left(1 - \frac{T_0}{T_k}\right) \dot{Q}_{ECMF}^{MF-} + T_0 \dot{S}_{irr,MF} \quad (5)$$

Using the same analysis for the system Ω_{ECMF} yields

$$\dot{W}_{ECMF}^{MF-} = \left(\dot{B}_{ECMF}^{E-fuel,ph} - \dot{B}_{ECMF}^{E-res,ph} \right) + \left(\sum_{i=1}^n b_{i,0}^{ch} \dot{N}_i \right)_{ECMF}^{E-fuel} - \left(\sum_{i=1}^n b_{i,0}^{ch} \dot{N}_i \right)_{ECMF}^{E-res} - \sum_{k>0} \left(1 - \frac{T_0}{T_k} \right) \dot{Q}_{ECMF}^{MF-} - T_0 \dot{S}_{irr,MF} \quad (6)$$

Here we have purposefully separated out the physical exergies, written as extensive quantities B , and the chemical exergies, where $b_{i,0}^{ch}$ represent the molar chemical exergies in the restricted dead state (2). We do this to emphasize the generality of this framework and the significant differences between two very important applications. In resource accounting, as done in life cycle analysis, the physical exergy terms are often ignored. Hence, the first term in parentheses on the right-hand side of eq 5 becomes zero because the material flows enter and exit the manufacturing process at the restricted dead state. However, many manufacturing processes involve material flows with nonzero physical exergies at system boundaries. To analyze these processes, and in particular to estimate the minimum work rate and exergy lost, these terms must be retained. This is typical for an engineering analysis of a thermodynamic system. Note that very similar equations can also be derived for the systems Ω_{MA} and Ω_{ECMA} . Before proceeding, it is worth pointing out several important insights from these results. First, in both eqs 5 and 6 we see that the magnitude of the work input is included fully while the heat inputs are modified (reduced) by a Carnot factor $(1 - T_0/T_k)$. Hence, in exergy analysis, work and heat are not equivalent, as they are in first law analysis. Second, eq 5 provides the framework for estimating the minimum work input for any process; i.e., when irreversibilities are zero, $T_0 \dot{S}_{irr} = 0$. The analytical statement formulated by eq 6 features all the energy interactions (including the energy carried by material streams) in terms of exergies, i.e., the available energy equivalents of all energy interactions. Such a balance may be written in general for an arbitrary open system Ω (including the one presented in Figure 1) as follows, see Figure 2:

$$\dot{B}_{in} + \dot{B}_{W,in} + \dot{B}_{Q,in} = \dot{B}_{out} + \dot{B}_{W,out} + \dot{B}_{Q,out} + \dot{B}_{loss} \quad (7)$$

In eq 7, the exergy components (i.e., exergy modes) of the balance are as follows:

(i) $\dot{B}_{in/out} = \dot{B}_{in/out}^{ph} + \dot{B}_{in/out}^{ch}$, (ii) $\dot{B}_{W,in/out} = \dot{W}_{in/out}$, (iii) $\dot{B}_{Q,in/out} = (1 - T_0/T) \dot{Q}_{in/out}$, and (iv) $\dot{B}_{loss} = T_0 \dot{S}_{irr}$. Work required beyond the minimum work, by definition, is lost. This represents exergy destroyed (\dot{B}_{loss}).

Electrical Exergy (Exergy) Used in Manufacturing Processes

Manufacturing processes are made up of a series of processing steps, which for high-production situations are usually automated. For some manufacturing processes many steps can be integrated into a single piece of equipment. A modern milling machine, for example, can include a wide variety of functions including work handling, lubrication, chip removal, tool changing, and tool break detection, all in addition to the basic function of the machine tool, which is to cut metal by plastic deformation. The result is that these additional functions can often dominate energy requirements at the machine. This is shown in Figure 3 for an automotive machining line (29, 30). In this case, the maximum energy

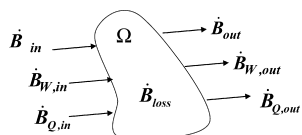


FIGURE 2. Diagram showing components of an exergy balance for any arbitrary open thermodynamic system.

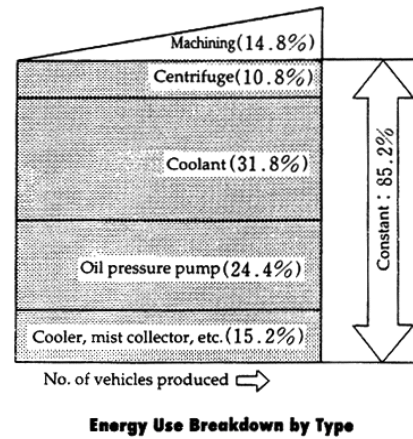


FIGURE 3. Electrical work rate used as a function of the production rate for an automobile production machining line (30).

requirement for the actual machining in terms of electricity is only 14.8% of the total. Note that this energy requirement represents an entity that is recognized in thermodynamics as a work interaction. At lower production rates the machining contribution is even smaller. Other processes exhibit similar behavior. See, for example, data for microelectronics fabrication processes as provided by Murphy (6). Thiriez shows the same effect for injection molding (20, 21). In general, there is a significant energy requirement to start-up and maintain the equipment in a “ready” position. Once in the ready position, there is then an additional requirement which is proportional to the quantity of material being processed. This situation is modeled in the following equation:

$$\dot{W} = \dot{W}_o + k \dot{m} \quad (8)$$

where \dot{W} = the total power used by the process equipment, \dot{W}_o = the “idle” power for the equipment in the ready position, \dot{m} = the rate of material processing in (mass/time), and k = a constant (J/mass). Note that the total power used by the process may alternately be presented as the exergy rate that corresponds to the electrical work. Hence, this equation is directly related to eq 5 for the work rate \dot{W} . Note that, with a model for the reversible work, one could directly calculate the lost exergy $T_0 \dot{S}_{irr}$ by comparing eqs 5 and 8.

The specific electrical work rate per unit of material processed, w_{elect} (J/mass), is then

$$w_{elect} = \frac{\dot{W}_o}{\dot{m}} + k \quad (9)$$

This corresponds to the specific or intensive work rate input (exergy rate) used by a manufacturing process. In general, the term \dot{W}_o comes from the equipment features required to support the process, while k comes from the physics of the process. For example, for a cutting tool \dot{W}_o comes from the coolant pump, hydraulic pump, computer console, and other idling equipment, while k is the specific cutting work, which is closely related to the work piece hardness, the specifics of the cutting mechanics, and the spindle motor efficiency. For a thermal process, \dot{W}_o comes from the power required to maintain the furnace at the proper temperature, while k is related to the incremental input required to raise the temperature of a unit of product; this is proportional to the material heat capacity, temperature increment, and enthalpies of any phase changes that might take place.

We have observed that the electrical power requirements of many manufacturing processes are actually quite constrained, often in the range 5–50 kW. This happens for several reasons related to electrical and design standards, process

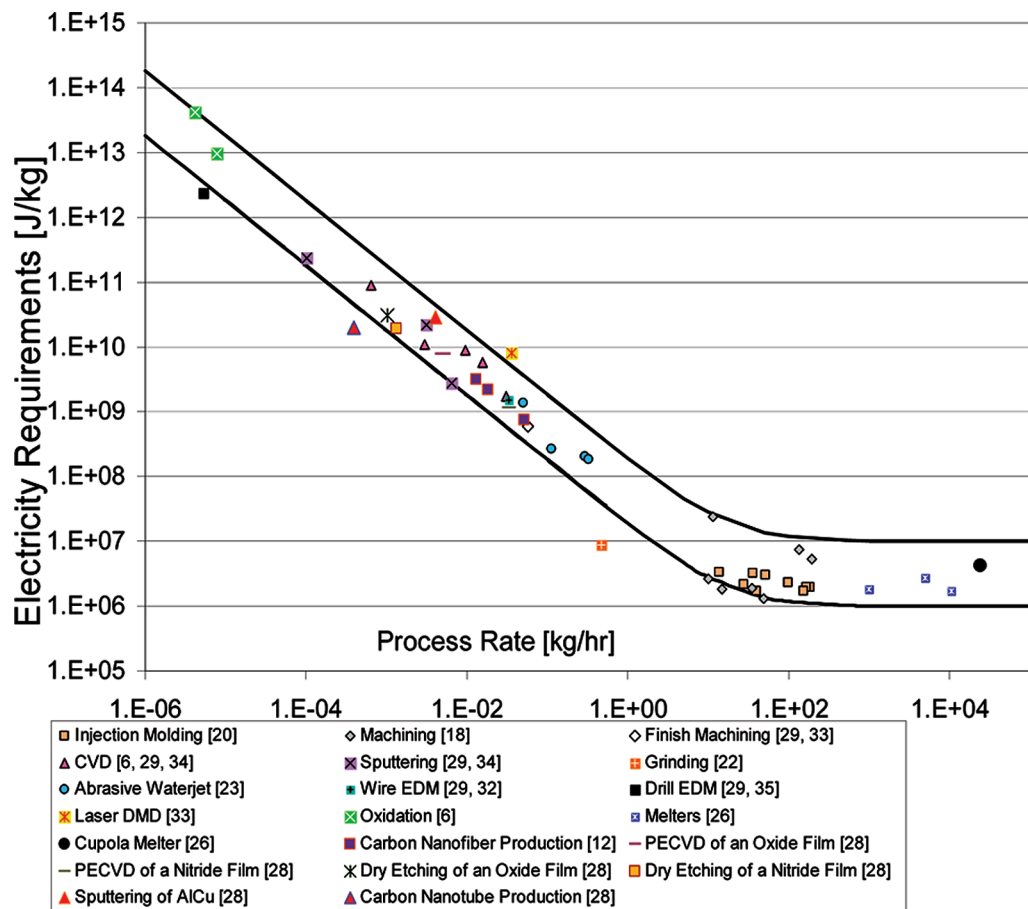


FIGURE 4. Work in form of electricity used per unit of material processed for various manufacturing processes as a function of the rate of material processing.

portability, and efficiency. On the other hand, when looking over many different manufacturing processes, we see that the process rates can vary by 10 orders of magnitude. This suggests that it might be possible to collapse the specific electrical work requirements for these processes versus the process rate on a single log–log plot. We have done this, and in fact the data do collapse, as shown in Figure 4 for 20 different manufacturing processes. (Note that the data for this figure are given in the Supporting Information.) What we see is that the data are essentially contained between four lines. The lower diagonal at 5 kW and the upper diagonal at 50 kW bound most of the data for the advanced machining processes and for the micro- and nanoproceses. The horizontal lines are meant to indicate useful references for the physical constant k . The lower one at 1 MJ/kg is approximately equal to the minimum work required to melt either aluminum or iron. The work to plastically deform these metals, as in milling and machining, would lie just below this line. The upper horizontal line approximates the work required to vaporize these metals. Somewhat surprisingly, nearly all of the data we have collected on a rather broad array of manufacturing processes, some of them with power requirements far exceeding 50 kW, are contained within these four lines. In the “diagonal region”, the behavior is described by the first term on the right-hand side of eq 9. At about 10 kg/h there is a transition to a more constant work requirement, essentially between 1 and 10 MJ/kg. This group includes processes with very large power requirements. For example, the electric induction melters use between 0.5 and 5 MW of power, and the cupola melter uses approximately 28 MW of power. Note that the cupola melter is powered by coke combustion and not electricity; hence, the power was calculated on the basis of the exergy difference between the

fuel inputs and residue outputs at T_0, p_0 according to eqs 5 and 6. This difference includes any exergy losses during the process.

The processes at the bottom, between the horizontal lines, are the older, more conventional manufacturing processes such as machining, injection molding, and metal melting for casting. At the very top of the diagram we see newer, more recently developed processes with very high values of electric work per unit of material processed. The thermal oxidative processes (shown for two different furnace configurations) can produce very thin layers of oxidized silicon for semiconductor devices. This process, which is carried out at elevated temperatures, is based upon oxygen diffusing through an already oxidized layer and therefore is extremely slow (6). The other process at the top (electrical discharge machining (EDM) drilling) can produce very fine curved cooling channels in turbine blades by a spark discharge process (35). Fortunately, these processes do not process large quantities of material and therefore represent only a very small fraction of electricity used in the manufacturing sector.

In the central region of the figure are many of the manufacturing processes used in semiconductor manufacturing. These include sputtering, dry etching, and several variations on the chemical vapor deposition (CVD) process. While these are not the highest on the plot, some versions of these processes do process considerable amounts of materials. For example, the CVD process is an important step in the production of electronic grade silicon (EGS) at about 1 GJ/kg. Worldwide production of EGS now exceeds 20 000 t, resulting in the need for at least 20 PJ of electricity (31). Notice also that recent results for carbon nanofibers are also in the same region (12). These fibers are being

proposed for large-scale use in nanofiber composites. Furthermore, carbon nanotubes and single-walled nanotubes (SWNTs) generally lie well above the nanofibers—by at least 1 order of magnitude (28) and possibility as much as 2 orders of magnitude or more (11). Hence, it should not be thought that these very exergy intensive processes only operate on small quantities of materials and therefore their total electricity usage is small. In fact, in several cases it is the opposite that is true.

When considering the data in Figure 4, keep in mind that an individual process can move up and down the diagonal by a change in the operating process rate. This happens, for example, when a milling machine is used for finish machining versus rough machining or when a CVD process operates on a different number of wafers at a time.

Note also that the data in Figure 4 may require further modification to agree with typical estimates of energy consumption by manufacturing processes given in the life cycle literature. For example, the data for injection molding, given by Thiriez, average about 3 MJ/kg. At a grid efficiency of 30% this yields a specific energy value of 10 MJ/kg. However, most injection molding operations include a variety of additional subprocesses such as extrusion, compounding, and drying, all of which add substantially to the energy totals. If these additional pieces of equipment are also included, they result in a value for injection molding of about 20 MJ/kg which agrees with the life cycle literature (14, 15, 20). Additionally, the data in Figure 4 do not include facility level air handling and environmental conditioning, which for semiconductors can be substantial (28).

Degree of Perfection for Manufacturing Processes

The exergy analysis of manufacturing processes, depending on the interactions involved, may or may not involve all or only some of the exergy modes (see eq 7). Note that eqs 5–7 show an exergy mode equivalence (as far as the additivity of this quantity is concerned) that allows us to aggregate work, heat, and material exergy. One should keep in mind that the exergies of different types may not have the same nonthermodynamic value (e.g., monetary value), but still may be aggregated. Material exergies can be viewed in two ways: (1) as a measure of the maximum work potential of the material with respect to a reference environment and/or (2) as a measure of the minimum work required to extract the material from the reference environment. This accounting scheme applies equally to fuels and nonfuel materials. In fact, many nonfuel materials such as metals, plastics, and highly reactive gases can have very high chemical exergies. When this dimension is added to the analysis, processes that refine chemical compounds and create pure components are given a credit for creating something of value, while those that destroy chemical exergy by mixing and reacting are given a deficit. Here we will apply this analysis to two examples using the so-called “degree of perfection” (5).

$$\eta_p = \frac{B_{\text{useful products}}}{B_{\text{inputs}}} \quad (10)$$

The numerator represents the material exergy of the useful output product produced by the manufacturing process. It should be mentioned that a figure of merit indicating a degree of perfection may be structured in a number of ways. Not a single representation is appropriate for all situations. In general, the most appropriate ones are characterized by the following requirements: (1) the numerator and denominator are both in terms of the same physical entity (exergy), leading to a dimensionless quantity, (2) the range of values spans the range between 0 and 1, and (3) the result should signify the objective of the analysis. In the case of eq 10, the denominator represents the exergy of the input materials

TABLE 1. Exergy Analysis of an Electric Induction Melting Furnace (26, 27)

input	mass (kg)	exergy (MJ)
Input Materials		
scrap metallics	0.68	5.08
cast iron remelt	0.30	2.51
additives	0.05	1.13
Input Energy		
electricity		1.72
total in		10.43
Useful Output		
gray iron melt	1.0	8.25
total out		8.25
degree of perfection (η_p)		0.79

TABLE 2. Exergy Analysis of a Plasma-Enhanced Chemical Vapor Deposition Process for an Undoped Oxide Layer (28)

input	mass (g)	no. of moles	specific chemical exergy (kJ/mol)	exergy (kJ)
Input Deposition Gases				
N ₂	276.3	9.86	0.69	6.80
SiH ₄	8.57	0.267	1383.7	369.4
N ₂ O	440.6	10.01	106.9	1070.2
Input Cleaning Gases				
O ₂	69.09	2.16	3.97	8.57
C ₂ F ₆	298.0	2.16	962.4	2078.1
Input Energy				
electricity				50516
total in				54049
Output				
undoped silicon dioxide layer	1.555	2.59E-02	7.9	0.204
total out				0.204
degree of perfection (η_p)				3.78E-06

(including work exergy in the form of electricity into the process). We will illustrate the magnitude of his figure of merit for two manufacturing processes at opposite ends of the material throughput spectrum. At the high production rate end, we analyze a batch electric induction melting furnace as used in the iron foundry industry (26, 27) (see Table 1), and at the low production rate end we look at plasma-enhanced chemical vapor deposition of silicon dioxide as used in the semiconductor industry (28). The materials and electricity exergy data and the results are given in Tables 1 and 2. The difference in efficiencies (almost 6 orders of magnitude) may not come as a big surprise given the previous results from Figure 4, but what is different is the use of very high exergy auxiliary materials in manufacturing processes which are not incorporated into the product. For example, in Table 2, one sees that the exergy of the input cleaning gases alone is more than 4 orders of magnitude greater than that of the product output. Furthermore, these gases have to be treated to reduce their reactivity and possible attendant pollution. If this is done using point of use combustion with methane, the exergy of the methane alone can exceed the electricity input (10, 29). When still other manufacturing processes are analyzed, one finds that while the degree of perfection is generally in the range of 0.05–0.8

for conventional processes, the range for semiconductor processes is generally in the range of 10^{-4} to 10^{-6} . Note that this analysis uses only the direct inputs and outputs to the manufacturing system given as Ω_{MF} in Figure 1. Hence, the exergy cost of extraction and purifying the inputs, which would be captured in the system Ω_{MA} in Figure 1, is not included in this analysis.

Discussion

In this paper we summarize trends on how energy and material resources are used in manufacturing processes. From the data in Figure 4 it is apparent that electricity use per unit of material processed has increased enormously over the past several decades. That is, the data in Figure 4 can be viewed in a chronological sense going from lower right to upper left. For example, note that processes such as machining and casting date back to the beginning of the past century and before, while the semiconductor processes were developed mostly after the invention of the transistor (1947) and the nanomaterials variations have come even more recently. The more modern processes can work to finer dimensions and smaller scales, but also work at lower rates, resulting in very large specific electrical work requirements. Furthermore, these processes make more use of high exergy value materials in very inefficient ways. These trends, of course, do not give the whole story for any given application. New manufacturing processes can improve and furthermore can provide benefits to society and even to the environment by providing longer life and /or lower energy required in the use phase of products. Furthermore, they may provide any number of performance benefits and/or valuable services that cannot be expressed only in energy/exergy terms. Nevertheless, the seemingly extravagant use of materials and energy resources by many newer manufacturing processes is alarming and needs to be addressed alongside claims of improved sustainability from products manufactured by these means.

At the same time this work provides a thermodynamic framework for the detailed investigation and improvement of these processes. For example, each of these processes discussed here can be analyzed component by component and compared to ideal reversible devices to identify inefficiencies and losses in the current systems. It should be pointed out that there is also a need for completely rethinking each of these processes and exploring alternative, and probably non-vapor-phase, processes.

Acknowledgments

We thank Dr. Delcie Durham and the National Science Foundation for their support through Grant DMI-0323426.

Supporting Information Available

Additional detailed information and references for the processes analyzed and presented in Figure 4. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Gyftopoulos, E. P.; Beretta, G. P. *Thermodynamics: Foundations and Applications*; Dover Publications, Inc.: New York, 2005.
- Bejan, A. *Advanced Engineering Thermodynamics*, 3rd ed.; John Wiley and Sons: New York, 2006.
- de Swaan Aarons, J.; van der Kooij, H.; Shankaranarayanan, K. *Efficiency and Sustainability in the Energy and Chemical Industries*; Marcel Dekker Inc.: New York, 2004.
- Sato, N. *Chemical Energy and Exergy—An Introduction to Chemical Thermodynamics for Engineers*; Elsevier: New York, 2004.
- Szargut, J.; Morris, D. R.; Steward, F. R. *Exergy Analysis of Thermal Chemical and Metallurgical Processes*; Hemisphere Publishing Corp. and Springer-Verlag: New York, 1988.
- Murphy, C. F.; Kenig, G. A.; Allen, D.; Laurent, J.-P.; Dyer, D. E. Development of parametric material, energy, and emission inventories for wafer fabrication in the semiconductor industry. *Environ. Sci. Technol.* **2003**, *37* (23), 5373–5382.
- Williams, E. D.; Ayres, R. U.; Heller, M. The 1.7 kilogram microchip: Energy and material use in the production of semiconductor devices. *Environ. Sci. Technol.* **2002**, *36*, 5504–5510.
- Krishnan, N.; Raoux, S.; Dornfeld, D. A. Quantifying the environmental footprint of semiconductor equipment using the environmental value systems analysis (EnV-S). *IEEE Trans. Semicond. Manuf.* **2004**, *17* (4), 554–561 (postprint).
- Zhang, T. W.; Boyd, S.; Vijayaraghavan, A.; Dornfeld, D. Energy use in nanoscale manufacturing. Presented at the IEEE International Symposium on Electronics and the Environment, San Francisco, CA, May 8–11, 2006.
- Boyd, S.; Dornfeld, D.; Krishnan, N. Lifecycle inventory of a CMOS chip. Presented at the IEEE International Symposium on Electronics and the Environment, San Francisco, CA, May 8–11, 2006.
- Issacs, J. A.; Tanwani, A.; Healy, M. L. Environmental assessment of SWNT production. Presented at the IEEE International Symposium on Electronics and the Environment, San Francisco, CA, May 8–11, 2006.
- Khanna, V.; Bakshi, B.; Lee James, L. Carbon nanofiber production; life cycle energy consumption and environmental impacts. *J. Ind. Ecol.* **2008**, *12* (3), 394–410.
- Morrow, W. R.; Qi, H.; Kim, I.; Mazumder, J.; Skerlos, S. J. Laser-based and conventional tool and die manufacturing: Comparison of environmental aspects. *Proceedings of Global Conference on Sustainable Product Development and Life Cycle Engineering*; uni-edition GmbH: Berlin, Germany, Sept 29 to Oct 1, 2004.
- Boustead, I. *Eco-Profiles of the European Plastics Industry: PVC Conversion Processes*; APME: Brussels, Belgium, 2002. http://www.apme.org/dashboard/business_layer/template.asp?url=http://www.apme.org/media/public_documents/20021009_123742/EcoProfile_PVC_conversion_Oct2002.pdf (accessed Feb 25, 2005).
- Boustead, I. *Eco-Profiles of the European Plastics Industry: Conversion Processes for Polyolefins*; APME: Brussels, Belgium, 2003. http://www.apme.org/dashboard/business_layer/template.asp?url=http://www.apme.org/media/public_documents/20040610_153828/PolyolefinsConversionReport_Nov2003.pdf (accessed Feb 25, 2005).
- Munoz, A.; Sheng, P. An analytical approach for determining the environmental impact of machining processes. *J. Mater. Process. Technol.* **1995**, *53*, 736–758.
- Mattis, J.; Sheng, P.; DiScipio, W.; Leong, K. *A Framework for Analyzing Energy Efficient Injection-Molding Die Design*; Engineering Systems Research Center Technical Report; University of California: Berkeley, 1996.
- Dahmus, J.; Gutowski, T. An environmental analysis of machining. Presented at the ASME International Mechanical Engineering Congress and RD&D Exposition, Anaheim, CA, Nov 13–19, 2004.
- Dalquist, S.; Gutowski, T. Life cycle analysis of conventional manufacturing techniques: Sand casting. Presented at the ASME International Mechanical Engineering Congress and RD&D Exposition, Anaheim, CA, Nov 13–19, 2004.
- Thiriez, A. An environmental analysis of injection molding. Project for M.S. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 2005.
- Thiriez, A.; Gutowski, T. An environmental analysis of injection molding. Presented at the IEEE International Symposium on Electronics and the Environment, San Francisco, CA, May 8–11, 2006.
- Baniszewski, B. An environmental impact analysis of grinding. B.S. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 2005.
- Kurd, M. The material and energy flow through the abrasive waterjet machining and recycling processes. B.S. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 2004.
- Cho, M. Environmental constituents of electrical discharge machining. B.S. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 2004.
- Kordonow, D. N. A power assessment of machining tools. B.S. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 2001.
- Jones, A. The industrial ecology of the iron casting industry. M.S. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 2007.

- (27) Branham, M.; Gutowski, T.; Sekulic, D. A thermodynamic framework for analyzing and improving manufacturing processes. Presented at the IEEE International Symposium on Electronics and the Environment, San Francisco, CA, May 19–20, 2008.
- (28) Branham, M. Semiconductors and sustainability: Energy and materials use in the integrated circuit industry. M.S. Thesis, Department of Mechanical Engineering, Massachusetts Institute of Technology, 2008.
- (29) Gutowski, T.; Dahmus, J.; Branham, M.; Jones, A. A thermodynamic characterization of manufacturing processes. Presented at the IEEE International Symposium on Electronics and the Environment, Orlando, FL, May 7–10, 2007.
- (30) Gutowski, T.; Murphy, C.; Allen, D.; Bauer, D.; Bras, B.; Piwonka, T.; Sheng, P.; Sutherland, J.; Thurston, D.; Wolff, E. Environmentally benign manufacturing: Observations from Japan, Europe and the United States. *J. Clean. Prod.* **2005**, *13*, 1–17.
- (31) Luque, A.; Lohne, O. *Handbook of Photovoltaic Science and Engineering*; John Wiley: New York, 2003.
- (32) Kalpakjian, S.; Schmit, S. R. *Manufacturing Engineering and Technology*, 4th ed.; Prentice Hall: Upper Saddle River, NJ, 2001.
- (33) Morrow, W. R.; Qi, H.; Kim, I.; Mazumder, J.; Skerlos, S. J. Laser-based and conventional tool and die manufacturing: Comparison and environmental aspects. *Proceedings of Global Conference on Sustainable Product Development and Life Cycle Engineering*; uni-edition GmbH: Berlin, Germany, Sept 29 to Oct 1, 2004.
- (34) Wolf, S.; Tauber, R. N. *Silicon Processing for the VLSI Era. Volume 1—Process Technology*; Lattice Press: Sunset Beach, CA, 1986.
- (35) McGeough, J. A. *Advance Methods of Machining*; Chapman and Hall: New York, 1988.
- (36) Valero, A.; Valero, A.; Arauzo, I. Evolution of the decrease in mineral exergy throughout the 20th century. The case of copper in the US. *Energy* **2008**, *33*, 107–115.
- (37) Dewulf, J.; Bösch, M. E.; De Meester, B.; Van der Vorst, G.; Van Langenhove, H.; Hellweg, S.; Huijbregts, M. A. J. Cumulative exergy extraction from the natural environment (CEENE): A comprehensive life cycle impact assessment method for resource accounting. *Environ. Sci. Technol.* **2007**, *24*, 8477–8483.
- (38) Hau, J.; Bakshi, B. Expanding exergy analysis to account for ecosystem products and services. *Environ. Sci. Technol.* **2004**, *38*, 3768–3777.

ES8016655