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PROJECT NEOS
A GENERAL STUDY OF PROCESSES FOR THE
REALIZATION OF DESIGN CONFIGURATIONS IN MATERIALS

Paul Rosenthal

CORNELL AERONAUTICAL LABORATORY

Contract: AF 33(600)-42921

ASD Project: NR 7-867

THIRD INTERIM TECHNICAL REPORT
3 APRIL 1962 TO 3 NOVEMBER 1962
CAL REPORT NO. NM-1559-P-3

Studies were continued within the framework of process elements established at the outset of the project and reported in the first interim report. Highlights are: (1) the concept of "embrittlement machining" based on one or more of several material embrittlement mechanisms discussed in the report and (2) recommendations for experimental investigation of surface hardening, oxidation retardation, and embrittlement of materials by ion bombardment. A summary of theoretical investigations, still in progress, on the application of dislocation theory to metal cutting and forming is included. An approach to process synthesis is outlined and related to immediate and long range Air Force needs.

MANUFACTURING TECHNOLOGY LABORATORY
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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In the section on energy considerations, the role of electric and magnetic fields as primary and as auxiliary energy sources is explored; to support the assessment of new and established applications, calculations of the forces, stresses, and energy and power densities are made. Electron, ion, and laser beams are compared, and their potential roles in material removal and material addition process are discussed. The mechanism by which electron beams penetrate materials and the power densities that are achievable are treated at some length. Experiments for exploring the corresponding characteristics of laser beams are recommended.

The embrittlement mechanisms mentioned above are evaluated systematically as part of the search for material modifications that can enhance material removal, addition, and displacement operations. Combination of the energy and material studies resulted in recommendations for ion bombardment experiments.

The effect of strain rate and temperature on material properties is investigated as part of the consideration of environmental effects in

manufacturing processes. The magnitude of strain rates in several manufacturing processes is calculated, and the concept of strain acceleration is explored. Dislocation behavior associated with strain is discussed in the continuing study.

Direct deposition processes, constituting one large class of material addition processes, are classified, and achievable mechanical properties and prospects of configuration control are discussed. Deformation processes, another large class in the process topology, are treated from the point of view of dislocation theory. A summary report that will be followed by a detailed development of theory and engineering applications is presented.

Finally, an approach to process synthesis is outlined and related to immediate and long-range Air Force needs.

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FOREWORD

This interim report covers the work performed under Contract AF 33(600)-42921 from 3 April 1962 to 3 November 1962. It is published for technical information only and does not necessarily represent the recommendations, conclusions, or approval of the Air Force.

The contract with the Cornell Aeronautical Laboratory, Inc., Buffalo 21, New York, was initiated under ASD Project NR 7-867, "A General Study of Processes for the Realization of Design Configuration in Materials." It is administered under the direction of Mr. W. M. Webster, ASRCTF, Manufacturing Technology Laboratory, Aeronautical Systems Division, Air Force Systems Command, United States Air Force, Wright-Patterson Air Force Base, Ohio.

Mr. Paul Rosenthal, Head of the Mechanical Engineering Section of the Laboratory's Applied Physics Department, is the project engineer. Others who cooperated in the research and in the preparation of the report were Mr. H. T. McAdams, Principal Physicist, Mr. W. R. Brown, Dr. N. S. Eiss and Mr. J. D. Myers of the Cornell Aeronautical Laboratory. The following persons participated as consultants to the project: Professor N. H. Cook of MIT, Professors H. H. Johnson and W. Pentland of Cornell University, and Professor B. F. von Turkovich, University of Illinois.

The primary objective of the Air Force Manufacturing Methods Program is to increase producibility and improve the quality and efficiency of fabrication of aircraft, missiles, and components thereof. This report is being disseminated so that those interested in the development of new manufacturing processes, the goal of the program, may participate in its progress from the outset.

Your comments are solicited on the potential use of the information contained herein as applied to your present or future production programs. Suggestions concerning your requirements for manufacturing methods development will be appreciated.

PUBLICATION REVIEW

APPROVED BY:

James W. Ford

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Applied Physics Department

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1. INTRODUCTION

Under Contract No. AF 33(600)-42921 for the Air Force Aeronautical Systems Division (ASD Project NR 7-867), Cornell Aeronautical Laboratory, Inc., is conducting Project NEOS, a systematic search to identify for further development new manufacturing processes.

Many of the unconventional approaches to manufacturing methods have arisen on an ad hoc basis, i. e., they have been addressed to producibility problems associated with specific materials in specific aerospace systems. As a result, there is an undesirable time lag in the development of manufacturing methods applicable to new materials. Project NEOS is aimed at eliminating this time lag by a systematic search for principles capable of leading to order-of-magnitude improvements in manufacturing processes.

To admit unconventional procedures, the definition of the term "manufacturing process" must be broadened to include the entire train of events from the time a material comes into being as a distinct substance until that substance is made to assume a desired configuration. Consequently, the project has as its objective an investigation of engineering materials at atomic, molecular, or other suitable levels and a determination of the kinds and magnitudes of energies required to produce useful configurations with acceptable properties and tolerances.

Several aspects of the manufacturing process are of interest: (1) the characteristics of the energy employed in transforming the material into the desired configuration; (2) the material from which the configuration is to be realized; (3) the environment required for the transformation to be effective, and (4) the means by which energy is applied to the material under adequate control for the process. In accordance with the systematic approach taken for the entire study, the main body of our report summarizes our program in each of the above categories in Sections 2 to 5. This summary is then followed by our approach to Synthesis, Section 6. Details of our studies are developed in separate Appendices, A to G.

2. ENERGY CONSIDERATIONS

Energy can affect matter either by changing its outward form or by modifying its physical properties. Both of these effects have potential for use in manufacturing processes. The following sections deal with the energy of electric and magnetic fields, of beams of free particles such as electrons and ions, and of certain forms of electromagnetic radiation.

2.1 Electric and Magnetic Field Effects

The strength of an electric field between two pole pieces is determined by the total flux and by the shape of the electrodes. High field strengths are obtained where the flux lines are closest together, namely near surfaces having small radii of curvature. When a material is placed in the field between the electrodes, the stresses in the body can be deduced from a field map. If the space between the electrodes is filled with a fluid dielectric and if the field is sufficiently high, dielectric breakdown occurs. It is this effect which initiates the work cycle in electric discharge machining.

Whereas high electric fields are characterized by the phenomenon of dielectric breakdown, a disruption of matter, there seems to be no parallel phenomenon in magnetic fields. Consequently, higher volume energy densities are obtainable in magnetic than in electric fields. Therefore, it appears that magnetic fields are more applicable for producing large forces in large bodies and that electric fields are more applicable for precisely regulated operations on small bodies. It should not be overlooked, however, that by a suitable coupling device the energy of an electric discharge can be distributed over a large area. Electrohydraulic forming affords a well-known example.

2.1.1 Control of Field Shape

The establishment of a field depends, practically speaking, on the establishment of equi-potential surfaces of specified geometry. These surfaces are on conducting materials for electric fields and on ferromagnetic surfaces for magnetic fields. Since relative resistivity has a much wider

range ($10^6/10^{-6}$) than permeability (5000/1) an electric field can be shaped more precisely than a magnetic field. The stresses developed in matter by electric and magnetic fields, and the energy and power densities capable of being realized, can be calculated from classical theory. In Appendix A the applicable theory is formulated and applied to typical manufacturing problems, and factors influencing the coupling of field energy to the workpiece are discussed.

To date most processes based on the energy of electric and magnetic fields have exploited the field energy as a primary energy source. Common characteristics of such processes are their peak power density, and the fact that energy densities produced in the workpiece are sufficient to produce failure in some sense. More subtle prospects for the use of field energy reside in its synergistic possibilities. In this mode of use, the energy of electric or magnetic fields affects the process primarily by modifying the physical characteristics of the material involved in the process. Thus the field energy cooperates with a primary source of energy in bringing about a change in material configuration.

2.1.2 Synergistic Possibilities

A systematic study of the prospects for using secondary effects of electric or magnetic energy in cooperation with other forms of energy to produce changes in material configuration is under way. The effect of electric fields on the yield strength and ductility of ionic crystals, as previously reported (1), is an example of the type of phenomenon presently under study.

The polarization of materials by electric or magnetic fields is of two types. If the domains, crystallites, or molecules of a substance have an inherent moment, they change orientation in an applied field. If the particles do not have an inherent moment, they are elongated in the direction of the field. The force supplied by the field is opposed by inherent microscopic forces in the material. Thus it is possible that a material subjected to alternating fields, by virtue of its state of agitation,

might be displaced by smaller applied mechanical forces than when no electric or magnetic field is applied. Further discussion of the effect of a modulated magnetic field on dislocation mobility is contained in Appendix G.

Since only very weak electric fields can exist in conducting bodies, electric field effects would be expected only in dielectric materials. Since many dielectrics of commercial importance are hard, refractory, and difficult to machine, any effect which facilitates deformation of the material would be useful. Consequently, experiments aimed at isolating such effects are warranted.

Magnetic polarization is very weak except in materials such as the alloys of iron, cobalt, and nickel, and in certain ferrite bodies. It is considered worthwhile to explore the effect of alternating magnetic fields on the workability of such materials. Any useful effects are expected to occur at frequencies in the audio or ultrasonic range, since skin effect at higher frequencies tends to shield the interior of the body.

Because of the lack of applicable theory in many of the areas of interest, a systematic search to discover the existence of useful synergistic effects must rely on a combination of theoretical and experimental methods. The desirability of such a search, however, is made evident by advances in such areas as ultra-high-strength magnetic fields, superconductivity, very high voltage sources, high power ultrasonic generators, plasma jets, and cryogenic techniques.

2.2 Electron, Ion, and Laser Beams

Electron, ion, and laser beams are relative newcomers to manufacturing technology, and their various fields of application have not been fully realized. In Appendix B an attempt is made to assess their potential roles on the basis of their physical characteristics for material removal and material addition. Though material displacement applications are not presently evident, such possibilities are not precluded.

The manner in which electron, ion and laser beams interact with materials dictates to a considerable extent how these energy sources are applied in manufacturing processes.

Because of the increasing use of electron beams in cutting and welding processes, the theory of these processes has received greatest attention. Their penetration depth and power densities are discussed in Appendix C.

The dominant mechanism by which energy transfer by electron beams takes place is the same for all materials. When high-velocity electrons impinge upon a material, they suffer collisions and, in the process, give up their kinetic energy to the material as heat. The shallow penetration of electrons in most materials is the specific property of electron beams which enables them to perform many of their unique functions. Energy density in the surface of the target material very quickly approaches the theoretical binding energy of the material. For this reason, electron beams have found ready application in cutting and welding processes. In the latter connection, it seems paradoxical that electron beams can make welds with depths up to 1 inch although penetration depths are less by perhaps 3 orders of magnitude.

According to current thinking, material immediately in front of the incident electrons is removed to allow for further electron penetration. A possible mechanism for such removal is the vaporization of subsurface areas and the consequent ejection of a stream of metal droplets from the weld cavity. This view is supported by calculations, performed under project NEOS and reported in Appendix C, in which the energy required to vaporize completely the volume of material in the weld cavity appears to be greater than the amount of energy available from the electron beam. Certain paradoxical aspects of that finding require further examination.

For manufacturing purposes, electron beams have a number of advantages. High powers can be concentrated into small areas, and by virtue of the fact that energy absorption is limited to a very small volume in the vicinity of the incident beam, there is very little distortion from heating effects. The beam can be readily shaped and controlled and its use in a programmed manner is entirely feasible.

The mechanism by which a laser beam removes material is quite similar to that of an electron beam. Both vaporize the material by generating intense heat within the target area. However, a laser beam can expose the target area to high-energy densities for shorter periods of time than can an electron beam. As a result, it has been reported that laser beams can drill holes with practically no oxidation along the walls of the machined areas regardless of the atmosphere. An experiment for studying the effect of a ruby laser beam on engineering materials is planned for execution during the next contract period.

Ion beams offer several advantages over electron beams for certain applications - for example, material removal and material modification. An ion beam removes material by sputtering rather than by vaporization; consequently, heat conduction is not a problem as it is in electron beam machining. Whereas an electron beam must be used in a pulsed manner, an ion beam could operate continuously. Further development of ion-beam machining requires new ion-beam devices capable of generating beams of sufficient power. The potential offered by ion beams for material modification is treated in Section 3.2.

3. MATERIAL CONSIDERATIONS

Material properties need not remain unchanged during a process; it is essential only that the material properties at the end of the process be consistent with the use concepts. In fact, the process might consist primarily of material modification, there being no appreciable change in configuration involved. The anodic treatment of aluminum surfaces, for example, is a case in point. In a broader sense, however, one may regard temporary modification of material properties as a means for facilitating cutting, joining, or deformation. Evidently, increasing either the ductility or the brittleness of the material could have considerable benefit for a manufacturing process. During the period covered by this report, particular attention was given to embrittling phenomena.

3.1 Material Modification by Embrittlement

Metals are known to be subject to embrittlement by several mechanisms. Several of these mechanisms and their relation to manufacturing processes are discussed below; a more exhaustive account is given in Appendix E.

Some single-phase metals, such as beryllium, are extremely brittle. Since chip formation in such materials is primarily a brittle fracture process, extremely brittle single-phase metals can be easily machined. The brittleness of beryllium is known to be due largely to the fact that only one crystallographic system of easiest slip exists in the hexagonal beryllium crystal. Thus it appears that if slip could be limited to one or two crystallographic planes, other metals or alloys might be similarly embrittled with a corresponding beneficial effect on machining performance.

Graphitic cast irons are examples of another class of easily machined materials. Their good machinability is largely attributed to the presence of discrete graphite flakes or nodules, which provide local stress concentration and paths of easy fracture. Thus the presence of a discrete second phase presents another possibility for embrittlement.

Many forms of gaseous embrittlement are known, hydrogen embrittlement being a well-known example. There appear to be at least three different ways in which hydrogen may embrittle metals. In the first, hydrogen is believed to react with a second phase at grain boundaries to produce severe intergranular damage. In the second, hydride compounds are formed internally, the result being essentially a second-phase embrittlement. Finally, there is the form of hydrogen embrittlement known in the titanium industry as low-strain-rate embrittlement, the mechanism of which is somewhat controversial. In addition to hydrogen, various other gases can produce embrittlement. For example, in some of the refractory metals, oxygen is believed to diffuse into the grain boundaries and there form an oxide of the parent metal. The result is an effect analogous to hydrogen attack.

In addition to the internal embrittling effect of gases, there is a type of surface embrittlement caused by stress in conjunction with the presence on metal surfaces of certain gases and liquids. Here the mechanism may be merely one of lowering the surface energy. The Griffith criterion for crack propagation is that the crack will grow only so long as the energy of the stress field around the growing crack exceeds the energy of the new surface created. Thus any mechanism which decreases surface energy would tend to foster crack growth. This type of embrittlement is frequently involved in stress corrosion, an example being the cracking of brasses in ammonia gas.

Other types of embrittlement include radiation embrittlement and low-temperature embrittlement. The bombardment of a material by particles such as protons, neutrons, or alpha particles is known to produce embrittlement, and body-centered cubic metals are known to undergo an abrupt change from ductile to brittle behavior upon cooling.

In Appendix E the various embrittlement mechanisms described above are compared with respect to their applicability to a machining process - thus the term "embrittlement machining." The criteria on which this comparison is based are: (1) generality of application; (2) severity, or degree of

embrittlement possible; (3) reversibility, or ease of recovery of toughness after embrittlement; and (4) controllability, or ease with which the embrittlement can be confined to a limited region. Some types of hydrogen embrittlement and liquid metal or other types of "environmental" embrittlement appear promising. In view of the lack of complete understanding of either embrittlement phenomena or machining mechanics, our studies must be supported heavily by experiments. Quite possibly a combination of two or more embrittlement treatments applied simultaneously might prove to be most effective.

3.2 Surface Modification by Ion Beams

According to a recent report of the Materials Advisory Board (2), a definite need exists for novel approaches to surface conditioning processes. In addition, the ability to modify material properties in a surface layer of material may afford a means for facilitating material removal by, e. g., chip-forming processes.

As a result of studies performed under project NEOS, it is concluded that ion beams have considerable potential for surface modification of materials. If the incident ions have sufficient energy, they will be incorporated into the surface layer of the target material. Thus high-energy ion beams conceivably could effect significant changes in material properties at the surface of a workpiece. Important classes of such modification are surface hardening, oxidation retardation, and embrittlement. The hardening mechanism could be of value in producing parts, such as bearings, in which hardened surfaces are required. Oxidation retardation is required in parts in which corrosion resistance is important. Both of these mechanisms are aimed at producing a final desired material characteristic in the workpiece. Embrittlement, on the other hand, would be most useful as an intermediate mechanism for facilitating a cutting operation. Since brittle failure characteristically involves less energy than ductile failure, surface embrittlement by ion beams could form the basis for an embrittlement machining process.

A general discussion of surface modification by ion beams is given in Appendix D and further thoughts on embrittlement machining in Appendix E. Commercially available and specially designed equipment for ion beam experiments are being evaluated. The formulation of plans for these experiments will follow.

4. ENVIRONMENTAL CONSIDERATIONS

In the context of project NEOS, the distinction between the principal energy applied to a material in a manufacturing process and the environment interacting with the material and the principal energy is arbitrary. In the previous reports, environment was defined as the set of all secondary or contributing influences that interact with the principal fabricating energies brought to bear on the material. In particular this definition includes the effects of pressure, temperature, rate of energy application, electric and magnetic fields, and polymorphic phase transitions, in addition to the process atmosphere. Progress is reported below on a study, still in progress, of the effect of strain rate on material properties and the applicability of these effects to producibility improvement.

4.1 Effects of Strain Rate and Temperature on Material Properties

Considerable publicity is being given to the high-energy-rate forming and machining processes which are being investigated and used to fabricate the new high-strength, high-temperature-resistant materials. Most investigators agree that the important parameter in high-energy-rate processes is the strain rate. The strain rate is determined by the material which is being processed. The physical properties of the material determine the speed at which stress waves travel and the size of the specimen determines the time required for the stress wave to return to the point of loading. Thus a strain rate which constitutes an impact loading rate for one material may be only rapid loading for another material.

Cottrell (3) illustrates the relation of rate of strain to material properties as follows: "... in materials we study there exist certain molecular processes which serve as pacemakers against which the applied rate of strain is to be compared, and ... when this rate becomes large, measured against one of these pacemakers, important changes occur in the process of deformation. This leads to a flexible classification of high and low rates of strain. For example, when soft copper undergoes plastic slip as a result of explosive loading,

the rate of strain ($\sim 10^5$ /sec) may be described from the standpoint of this molecular process as 'low.' But no matter how slowly a rod of cold glass is bent to fracture, the rate of strain remains 'high' in the sense that the deformation takes place too quickly to permit plastic flow to occur. So-called 'elastic' solids are in fact those for which conventional rates of strain are too high for plastic flow. "

Increasing strain rate and decreasing temperature have qualitatively similar effects on mechanical properties of metals such as ultimate strength of flow. Because of this similarity, single-valued relations between the two have been proposed by various investigators. For steel in the vicinity of room temperature, a decrease of 110 degrees in testing temperature T is approximately equivalent to increasing the strain rate by a factor of 1000.

Temperature affects the mechanical properties of a metal in two ways: (1) by modifying the structure of the metal and (2) by controlling the extent to which the several possible modes of deformation will be operative. At low temperatures brittle-type failure is common; at high temperatures creep predominates. For some metals, such as low-carbon steel and molybdenum (0.5 percent Ti), the transition from brittle to ductile behavior occurs over a very narrow temperature range, called the transition temperature range. Increasing the strain rate causes the transition temperature to rise. In the transition temperature range some structural change in the material occurs such that the high-temperature structure has a greater number of slip planes than the low-temperature structure. The high strain rates inhibit the structural change in some manner which results in a rise in the temperature at which the structural change occurs. The interaction of strain rate and the structural changes can be further investigated through solid-state physics theory.¹

The brittle-ductile transition range is normally measured by the energy required to fracture a specimen as a function of temperature. We have

¹Efforts in that direction are discussed in Appendix G.

already noted that increasing of strain rates causes a decrease in the energy required to fracture. Another material property closely related to the energy required to fracture is the toughness of the material. W. W. Wood (4) has postulated that as the strain rate is increased, the toughness of the material reaches a maximum and then decreases. He then says that for high-velocity forming techniques, the material has to have high toughness, and the strain rate that gives maximum toughness for the material should be selected. He also postulates a similar relation between temperature and toughness and indicates that there is an optimum temperature for maximum material toughness. It must be emphasized that Wood's statements are based on qualitative stress-strain curves. An experimental follow-up that would yield quantitative data appears worthwhile.

When the above strain-rate effects are examined for pertinence to our producibility concepts, the one effect which seems to hold the most promise is the effect of strain rate on the brittle-ductile transition temperature. We have already determined that for metal displacement operations a material should be ductile, whereas for metal removal operations it should be brittle. Hence, by manipulation of strain rates and temperatures, it should be possible to control the ductile-brittle behavior of materials which exhibit these two properties to best enhance the process being used.

A limited search for data on the effects of strain rate on material properties revealed that in most cases order-of-magnitude changes in ductility, yield strength, ultimate strength, and toughness have not been observed. Data on both ferrous and nonferrous alloys indicated that increasing the strain rate from 10^{-4} /sec (static tests) to 10^4 /sec (impact tests) for temperatures well below the melting point increased the yield strength of the materials by a factor of three at most. Though order-of-magnitude improvements in producibility through manipulation of the strain rate are not to be expected, appreciable improvements are possible for some materials.

4.2 Strain Rates in Various Processes

One common misconception about the high-energy-rate processes is that the strain rates produced are so high that a substantial modification in the

properties of the material occurs. However, calculations of strain rates show that, while they exceed those in many deformation processes, they are about as large as those in metal cutting and much less than those in grinding. Estimates of strain rates in some processes are given below.

Strain rate in metal cutting operations has been estimated by several investigators who made different assumptions about the thickness and shape of the sheared layer of metal. All the estimated strain rates are of the same order of magnitude; only one such calculation is given here.

Drucker (5) defined strain rate as strain divided by the time required to traverse the shear zone.

$$\dot{\epsilon} = \frac{\epsilon}{t}$$

where

$$t = \Delta y / V' = \Delta y / V \sin \theta$$

V = cutting velocity

Δy = mean value of spacing for successive slip planes.

θ = shear angle

Drucker estimates that the thickness of the shear zone is at most 1/20 the depth of cut. Assuming $V = 200$ ft/min, $\theta = 15^\circ$, depth of cut = 0.01 in., and strain $\epsilon = 2$, he calculates the strain rate to be 4×10^4 /sec.

In grinding operations the depth of cut is normally an order of magnitude less than in other metal-cutting operations. If we assume that the thickness of the sheared layer is unaffected by the depth of cut, until they are both the same order of magnitude, then we can estimate that the thickness of the sheared layer in grinding would be about equal to that in metal cutting. However, grinding speeds (ranging from 1000 to 10,000 sfpm) are one to two orders of magnitude higher than in metal cutting. Strain rates in grinding would therefore be 10^5 to 10^6 /sec.

In both grinding and metal cutting the temperatures at the cutting interface are high, especially for heavy cuts and high speed. Since, as we

have noted, increasing temperature and decreasing strain rate have the same effect on material properties, the temperature rise during cutting counteracts the benefit from the high strain rates. Thus, in first approximation the material in these operations is assumed to behave according to its room-temperature, static stress-strain curve. Attempts have been made to exploit the strain rate effect on material properties by cooling the tool and workpiece to subzero temperatures during machining to keep the rise in temperature from canceling the strain-rate effects. The beneficial increase in tool life in subzero machining experiments may be attributed to either the lower energy required for machining or to the decreased wear of the tool at the lower temperature.

Strain rates in materials subjected to shock waves such as those produced by explosives have been estimated by calculating the strain and dividing by the rise time of the shock wave. The strain was calculated by assuming that as a longitudinal shock wave passed through a rectangular element of the material, the element suffered a contraction in the direction of the shock and that the other dimensions remained unchanged. The strain accompanying this dimension change can be related to the change in density of the material by the following expression:

$$\epsilon = 1 - (\rho_0/\rho)$$

where ρ_0 is the initial density and ρ is the density of shocked material. Typical strain rates reported are given in Table 1.

TABLE 1
DYNAMIC PROPERTIES OF METALS SUBJECTED TO SHOCK WAVES (6)

Material	Ratio of Dynamic- to-Static Yield	Strain Rate
SAE 1020 Steel	2.6	$> 10^4$
Mild Steel	2.9	$> 2 \times 10^4$
SAE 1040 Steel	1.8	$\geq 2.4 \times 10^3$
2024-T4 Al	.96	$> 6 \times 10^4$
2024-T4 Al	.45	$> 7 \times 10^3$

From the above data we can see that strain rates computed for metal cutting and some explosive loading conditions are comparable in magnitude. The nature of the strain is not the same in each case. In metal cutting the strain is a shear strain, whereas the strain in the calculations of the strain rate in shock waves is compressive. The relation of these different strains and strain rates to material properties must be understood so that valid comparisons can be made between strain rates in different processes. Continuation of our investigation is planned.

4.3 Dislocation Concepts and Strain Rate

Considerable data exist on the effect of strain rate on the macroscopic properties of the materials. Much less is known on the microscopic scale. One approach to a more basic understanding of the strain rate phenomena is through dislocation theory. In this context, strain rate can be approximated by the following equation:

$$\dot{\epsilon} \cong L b v_d$$

where L = number density of moving dislocations
 b = Burgers vector magnitude, a material constant
 v_d = dislocation velocity

The maximum theoretically possible strain rate depends on the maximum number density of dislocations and the maximum velocity of the dislocations. For a number density of $10^{12}/\text{cm}^2$, Burgers vector magnitude of 10^{-8} cm, and a dislocation velocity equal to the velocity of the shear-wave velocity in the material, 10^5 cm/sec, the maximum theoretical strain rate is $10^9/\text{sec}$. Actually, such a rate is unobtainable owing to the phenomenon of dislocation annihilation which occurs for high densities.

Most investigators believe that dislocation velocity is limited to the velocity of the shear-wave velocity in the material. Dislocations moving faster than the shear-wave velocity have not been observed. Nevertheless,

the possibility of the existence of dislocations, the propagation of which proceeds with velocities greater than that of the shear wave in the material is held out by a few investigators.

Eshelby (7) envisioned the supersonically propagated dislocation as a portion of a crystal in which the atoms immediately above and below the slip plane are in a state of complete misfit. The passage of the dislocation restores the proper fit. How this type of dislocation moved "supersonically" is best illustrated in the sketch below.

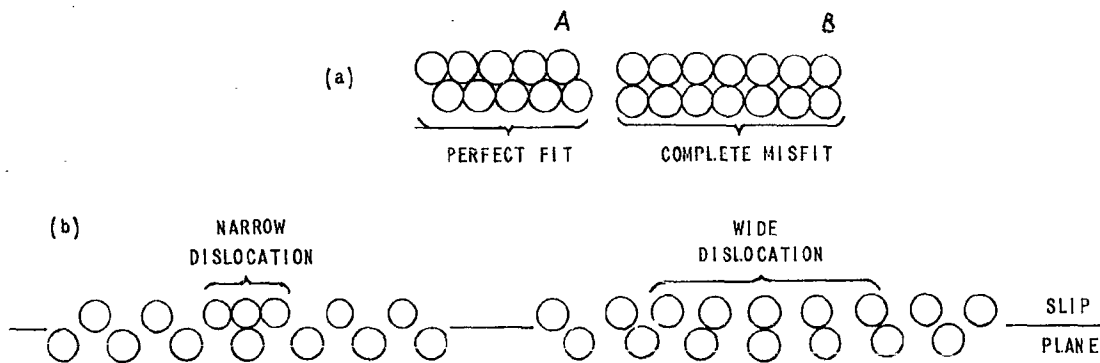


Figure 1 DISLOCATION MOVEMENT

If the block of atoms between A and B in Figure 1a drops into perfect fit simultaneously, the dislocation at A appears to move to B infinitely fast. Thus, any "apparent" dislocation velocity is possible depending on the rate at which the misfit atoms move into perfect fit. In Figure 1b, a conventional subsonic dislocation movement is illustrated and we see that the supersonically propagated dislocation could be considered as a special case of a dislocation with a wide core where the core is defined as the region in which the atoms lie in the middle half (from $1/4$ to $3/4b$) of their total slip displacement b . In the supersonically propagated dislocation, the region from A to B could be considered the dislocation core in which all atoms are slipped $1/2 b$. The movement of the block of atoms A to B into complete fit is a gross slip type of movement from a half-slipped position.

If dislocations can indeed propagate supersonically, then their relative importance in macroscopic phenomena must be assessed. Supersonically propagated dislocations must move on planes in the crystal which give up energy to the dislocations. These planes, such as those where there is a complete misfit of atoms across the plane, are few in number compared to the possible planes on which dislocations can move subsonically. Thus, the number of supersonically propagated dislocations would be small. It is possible, however, that, under unusual situations such as in shock waves, conditions would favor supersonic propagation of dislocations, and hence this mode would assume some importance. Further development of dislocation theory as it relates to strain rates will be followed closely.

4.4 Strain Acceleration

In the high-energy-rate processes where the shock waves pass in microseconds, it has been suggested that the rate of change of the strain rate, or strain acceleration, and its effect on the material properties might be important. If we consider strain as a manifestation of dislocation movement as discussed above, then we must also consider the acceleration of dislocations.

Campbell et al. (8) demonstrated that because of their extremely small inertias, dislocations achieve their maximum limiting velocities in about 5×10^{-10} sec. At this time the estimated plastic strain in a crystal containing the usual number of dislocations is about 0.3 percent. Materials loaded by shock waves are subjected to different conditions than those provided by the impact tests. Smith (9) estimates the shock front thickness at no more than 10^{-3} cm. At a wave velocity of 5 mm/ μ sec, the required density change must occur in 10^{-9} sec. This time is of the same order of magnitude required for dislocations to accelerate to their maximum velocity so that the influence of the strain acceleration on the resulting material behavior may be significant.

As a more complete understanding of the dislocation mechanisms in material deformation is obtained, we will be better able to assess the importance of strain-rate control as a means of improving producibility. The

most promising area is the understanding of the high-rate deformation processes for which dislocation theory has not been developed. As the theory evolves, it may point the way to areas where significant changes in producibility can be obtained.

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5. TOPOLOGICAL CONSIDERATIONS

Manufacturing processes can be classified according to the sequence of configurational changes which a material undergoes during the manufacturing operation. In essence, this sequence of events can consist either of adding, removing, or relocating material, as indicated schematically in Table 2. For purposes of process generalization, it is appropriate to consider either the various topologies applicable to particular energy sources, or to consider the various energy sources amenable to particular topologies. The comparison of electron, ion, and laser beams in Appendix D affords an example of the first approach. Appendix F, which presents a broad survey of direct-deposition processes, is an example of the second.

TABLE 2
PROCESS TOPOLOGY

I	Volume-Preserving Processes
1)	Intensive Processes (Forging ^a)*
2)	Extensive Processes (Casting ^a , Powder Metallurgy ^b)
II	Volume-Nonpreserving Processes
1)	Material Removal
a)	By Momentum Transfer (Ion-Beam Machining ^a , Milling ^a)
b)	By Vaporization (Electron-Beam Machining ^a , Optical Masers ^b)
2)	Material Addition
a)	Discrete Joining (Solid State Bonding ^{a, b})
b)	Continuous Joining (Crystal Growth ^a)

*Superscripts a and b denote examples of each process as discussed in the First and Second Interim Technical Report, respectively.

5.1 Direct Deposition Processes

The types of structures produced by available direct-deposition methods are discussed with respect to mechanical property and configuration control factors. A survey of the kinetics of direct-deposition processes, such as crystal growth, is in progress and will be completed in the next contract period. The survey is expected to provide insight for further application of direct-deposition concepts.

Directly deposited self-supporting structures and coatings are formed by continuously additive processes. The added units may be atoms, molecules, droplets, or solid particles. Most direct-deposition methods fall into five categories: (1) growth from melts; (2) growth from solutions; (3) growth from vapors; (4) deposition from suspensions; and (5) hot spraying.

Growth from melts includes any processes by which single or polycrystalline materials are grown with the growth interface in contact with molten material of the same composition. Typical methods include pulling a crystal out of the melt and the use of a floating zone of melt held in place by surface tension.

Strictly speaking, all melts are solutions since there is always some impurity present. Therefore, one can consider crystal growth from either the solvent or the solute phase. Thus, melt growth constitutes growth of the solvent phase. Growth from solution, however, is usually understood to mean precipitation of the solute phase onto a seed crystal. Applicable methods include cooling of super-saturated solutions, electrolytic plating, and catalytic reduction.

Growth from vapors is achieved by thermal evaporation in a vacuum of a stream of atoms or molecules. The vapor is then caused to condense on a cool surface. Processes involving the decomposition of a volatile compound have been referred to as molecular forming processes.

Fine particles of solid materials suspended in liquids or gases can be deposited in a controllable manner. Simple examples are spraying and

dipping. By means of hot spraying, it is possible to propel molten droplets of a solid material to a substrate surface.

An important consideration in direct-deposition processes, as it is in all processes, is the type of material structure which can be obtained by these methods. In many instances, these considerations constitute severe limitations to the utilization of a given process. Further detail on the types of structure realizable by the various methods discussed above, as well as control possibilities, are presented in Appendix F. Although process rates, in many instances, appear to be limited, the actual worth of any process must be evaluated from a broad base of criteria. As will become evident in Section 6, a low process rate may be tolerable if it is impossible to produce the desired material structure by any other means.

5.2 Deformation Processes

The need for understanding the plastic deformation of materials on a microscopic scale was discussed in the First Interim Technical Report (Section 6.1.2) and is again apparent from the investigation of strain-rate effects discussed in Section 4 of this report. The current NEOS study has as its goal a unified statement of the theory of dislocations and point defects. The theory is then applied to deformation processes of interest. We believe that the study, by opening up a new understanding of deformation behavior, will provide new approaches in the search for possible manufacturing processes. A summary of the effort is presented in Appendix G.

6. EVALUATION AND SYNTHESIS

Project effort thus far has been aimed primarily at identifying physical phenomena which might be exploited in the development of novel processes. Actual postulation of such processes, however, implies that these phenomena be viewed in a new light relative to existing technology. Hence it becomes more and more imperative to look toward the synthesis of process elements into novel combinations and in particular, to seek combinations which could conceivably lead to order-of-magnitude improvements over the present state of the art. Inasmuch as few, if any, existing processes are "simple," in that they rely exclusively on a single physical principle, it becomes increasingly necessary to consider energy forms, topologies, etc., in unfamiliar combinations. Thus a sort of "systems approach" to manufacturing process development is indicated. In such an approach, feasibility considerations must go beyond single elements and must encompass complexes in which various process elements combine to assist each other toward a workable process.

The direction which such synthesis will take must be based, to a large extent, on critical Air Force needs. Hence, efforts to formulate new processes, to be most effective, must be directed toward those fabrication problems which, at present and in the immediate future, tend to frustrate the aerospace research and development program.

In the following sections, an approach to process synthesis will be outlined and discussed in relation to both immediate and protracted Air Force objectives.

6.1 Process Synthesis

In any manufacturing process, whether additive, subtractive, or volume preserving, there is a change in material configuration, this change being brought about by an energy input from the environment to the workpiece system. (See Figure 2.)

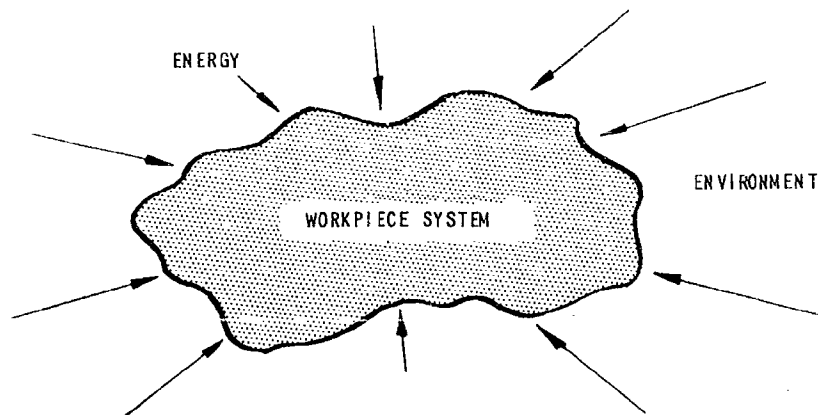
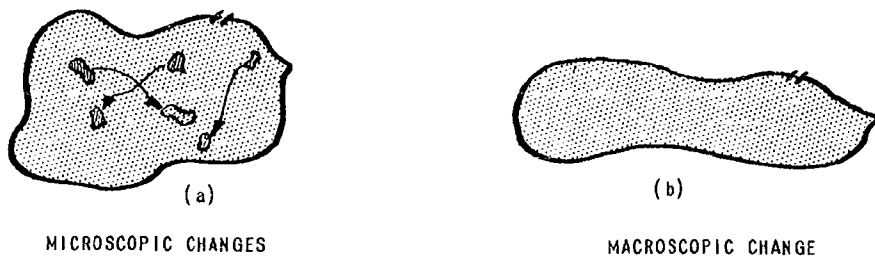


Figure 2 RELATION OF WORKPIECE TO ENVIRONMENT

Changes in material configuration can be considered at either the microscopic or macroscopic level. By a microscopic change is meant material organization which does not affect the macroscopic shape of the object under study but which may appreciably change overt material properties. In such transformations, internal elements of the material change relative positions without changing the relation of surface elements to a fixed point inside the piece (see Figure 3a). By a macroscopic transformation, on the other hand, is meant one which produces sensible changes in configuration as viewed from an external point (see Figure 3b).



MICROSCOPIC CHANGES

MACROSCOPIC CHANGE

Figure 3 EFFECT OF ENVIRONMENT ON WORKPIECE SYSTEM

During a change in configuration, energy is redistributed. Input energy can be absorbed either intensively or extensively. Intensively absorbed energy goes to produce material reorganization on only a microscopic level, whereas energy absorbed extensively goes to produce geometric changes on a macroscopic scale. Microscopic changes can be either desirable or undesirable; in many cases, however, energy absorbed intensively produces such undesirable effects as work hardening, which tends to limit further geometric deformation.

The partitioning of input energy into microscopic and macroscopic energy-absorbing mechanisms can be controlled by controlling the form in which energy is introduced into the system. Thus, under suitable conditions it should be possible to minimize material modification and maximize deformation or vice versa. Accordingly, it should be possible to realize varying degrees of synergism in manufacturing processes.

Synergistic mechanisms are energy-exchange processes which in some sense favorably affect the energy partition between microscopic and macroscopic absorption. For example, dislocation mobility is a factor affecting the absorption of energy by plastic deformation. Means of introducing energy so as to increase mobility, therefore, should have a synergistic influence on the fraction of input energy which can be utilized for deformation purposes. Consider, for example, the effect produced by heat in a forming operation. Raising the temperature of the workpiece may reduce the flow stress by an order of magnitude, with a consequent reduction in the amount of mechanical energy needed to form the piece. Though it may be necessary to add a considerable quantity of heat to raise the temperature of the piece, most of this heat can be recovered upon cooling to the ambient temperature. Thus, from the standpoint of energy balance, the use of heat energy to replace part of the mechanical energy produces a highly synergistic effect.

Every crystalline solid material has a definite lattice energy, the energy required to separate the ions of a crystal to an infinite distance from each other. Hence, the energy required in the reorganization of a unit volume of material to achieve a design configuration can be of an order of magnitude no greater than the storage density of chemical energy, since such reorganization requires the breaking of chemical bonds. If one pursues this argument,

it is evident that energy densities exceeding the lattice energy of a crystal, wherever and however realized, must certainly have potential for material processing, provided, of course, that adequate control of the applied energy can be realized. For example, in sufficiently high magnetic fields, materials can be subjected to energy densities exceeding those realized in high explosives, a fact which forms the basis for magnetic forming.

Energy concentrations equal to or exceeding the lattice energy are sufficient to affect materials in a manner possibly favorable to process development. However, such high concentrations of energy, at least in one particular form, may not be necessary. As the energy density increases and approaches the binding energy, the cohesiveness of the material must decrease accordingly, though not necessarily in a regular or systematic way. Discrete steps, such as phase changes, may occur, or there may be a gradual softening of the material with increase in energy stored. Such effects as the latter may be exploited by applying a second form of energy to achieve synergism.

For example, it was reported in the second interim report that the yield strength of materials can be reduced by high electric fields, and that the effect can not be attributed entirely to heating (10, 11). These observations suggest that the field must interact with the dislocations and point defects important in plastic flow. Gilman and Stauff suggest that dislocations nucleated in LiF crystals by electric fields result from the high mechanical stresses induced by such fields (12). Also in this connection, Cooper and Wallace found that, in experiments designed to measure the electric strength of KCl, errors were introduced by strains resulting from the electric field. They further noted a relation between electric strength and the extent of work hardening (13).

Benefits which conceivably might arise from the use of a modulated magnetic field in metal cutting are discussed in Appendix B. It is postulated that by application of such a field it might be possible to enhance dislocation mobility and thereby facilitate chip formation.

Various energy effects resulting from the combined action of two or more forms of energy on materials were discussed in a previous interim report on Project NEOS (14). Those effects, however, by no means exhaust the possibilities expected to be disclosed in our systematic search for cooperative mechanisms.

Though classification of forms of energy is to some extent arbitrary, one recognizes at least mechanical, chemical, thermal, electrical, and magnetic energy as having specific and identifiable effects on materials. Though these effects are interrelated in such a way that their complete separation and isolation is never realized, each is subject to varying degrees of emphasis in existing and proposed processes.

The manner in which these various forms of energy are interrelated can be illustrated as shown in Figure 4, though a complete picture would require visualization in five-dimensional space. In this figure, vertices represent processes in which only one form of energy predominates. Edges represent energy couples, such as are involved in, say, electromechanical, thermoelectric, and mechano-chemical effects. Faces (triangles) and tetrahedra represent situations in which, respectively, three or four forms of energy cooperate. An example is found in stress corrosion cracking, in which electrochemical activity is accelerated by mechanical stress. Finally, the entire configuration represents a situation in which all five forms of energy are involved.

A microscopic characterization of interactions among the various forms of energy requires a field description of the phenomena involved. With such field descriptions available, the evolving of new processes could be reduced to the status of engineering design. It is regarded as the objective of this project to provide not only specific examples of new processes but a modus operandi for the evolution of new processes as needs arise.

The classic equations of Maxwell provide a characterization of electric and magnetic fields and their interaction. As shown in Appendix A, these equations lead to a tensor formulation of mechanical forces due to electric and magnetic fields. Similarly it is possible to discuss in field concepts such galvanomagnetic, thermomagnetic, and magneto-resistive effects as the Hall, Nernst, Righi-Leduc, and Ettinghausen effects (15). Dislocation theory as discussed in Appendix G, provides a field description of stresses and strains in materials, but further development is required to describe the interaction of stress fields with electric and magnetic fields. Finally, further

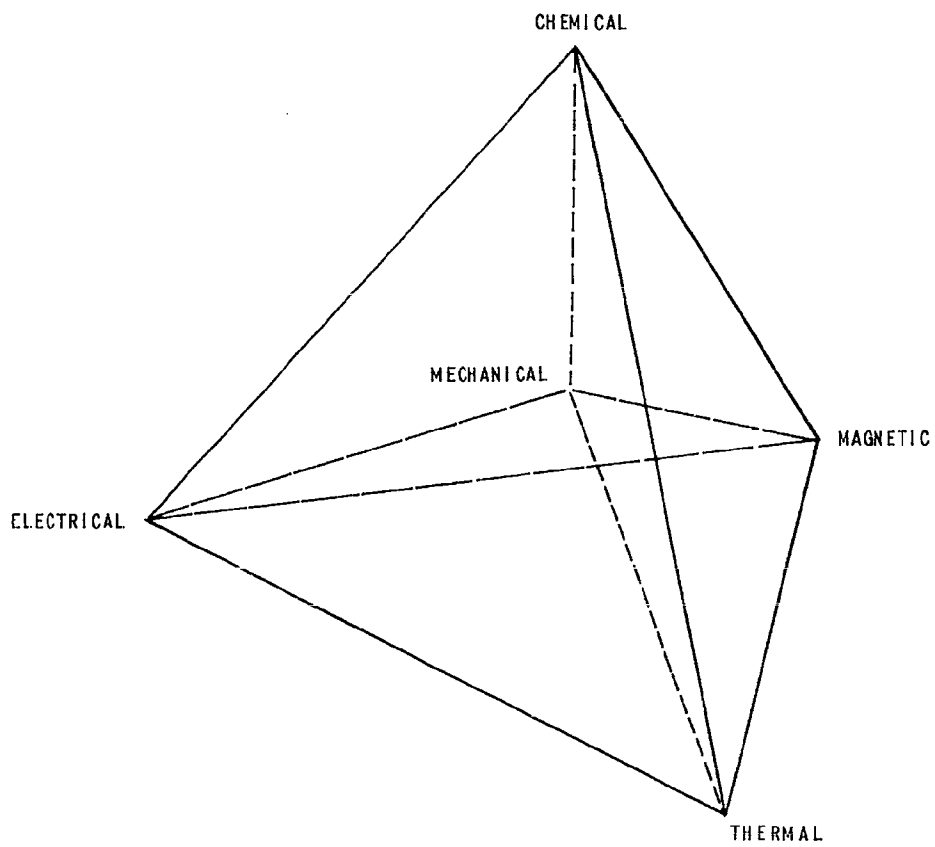


Figure 4 INTERRELATION OF PROCESS ENERGIES

clarification of the role played by chemical reaction and how such reactions respond to superimposed thermal, electrical, magnetic, and stress fields is required.

The exploitation of synergism may imply time sharing of two or more forms of energy or perhaps of two or more entire sequences of operations or topologies. The time-sharing aspect is evident in such manufacturing processes as metal processing. A forming operation predominantly effected by mechanical energy may be followed by annealing (thermal energy), and the process may be repeated a number of times until the desired configuration and material properties are achieved. In this case the period of the time-sharing cycle is relatively long -- so long, in fact, that the time-sharing feature of the process topology may not be specifically recognized. In the interest of generalization, however, one can conceive of processes in which the basic cycle may be quite short, on the order of, say, milliseconds, and of course in the limit one could say the several forms of energy were applied simultaneously.

The possibility of short-period (high-frequency) time-sharing of energy forms is suggested by such novel forms of energy as those supplied by electron beams, lasers, and so on. By scanning and blanking techniques, it is conceivable that very small parts of the workpiece could be sequenced systematically through exposure to various forms of energy in a programmed manner to achieve a desired configuration.

For example, it is noted that electrophoretic deposition as a direct transformation process is limited by the need for isometric pressing and sintering to consolidate the "green" body. Suppose, however, that it were possible to consolidate the body "continuously" during deposition. Such consolidation might be achieved by consolidating one site while deposition were occurring on another. For example, an electron or laser beam suitably programmed might systematically sweep the surface of the body and, by virtue of the high local temperatures produced, liquefy the porous deposit and weld it to the growing body. In the meantime, provided suitable sequencing could be achieved, other sites might have a temperature and/or charge distribution favorable to deposition. Even an additional form of energy, say mechanical

energy, might be included in the sequence to remove from certain sites deposits intentionally not consolidated into the configuration. Thus, one might combine both addition and subtraction into the same topology in a manner advantageous to the process as a whole. The frequency limits of time-sharing in the present state of the art can be inferred from such applications as radar and other data-processing systems, digital computers, and so on. From this standpoint, cycle control in the order of microseconds is at least conceivable.

6.2 Air Force Requirements as a Guide to Synthesis

The worth of a proposed new process may be regarded abstractly as shown in Figure 5.

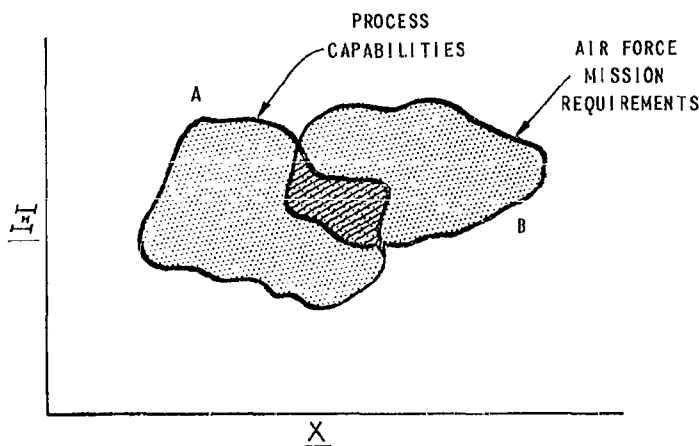


Figure 5 PROCESS AND MISSION DOMAINS

In this figure, the domain A represents the collection of all design vectors $\underline{X}$ and tolerance vectors $\underline{T}$ capable of being realized by the process; the domain B represents the collection of all design vectors $\underline{X}$ and tolerance vectors $\underline{T}$ for which there is an Air Force requirement. The intersection

(shaded area) of these two domains in the region within which the process has potential for satisfying Air Force needs, and it is within this framework that the process must be evaluated by means of appropriate criteria. In general, it is probable that one process will be better than another in some respects and worse in others, and that a given system will be worthwhile for certain applications but not for others. Evaluation must be based on a set E of characteristics indices $\{e_1, e_2, \dots, e_r\}$ where e_1 may be a cost factor, e_2 may be a time factor, and the remaining indices are factors based on other appropriate considerations, each appropriately weighted. It should be noted, of course, that the region of usefulness of a process in the (X, E) space might be as small as a single point. For example, a process for drilling very small holes with close tolerances in a specific material might be a very worthwhile development, particularly if this satisfies an Air Force requirement which cannot be met by any other means.

An assessment of current Air Force requirements in the field of material processing can be obtained from the Phase III Report of the Aircraft and Astronautics Panel of the Materials Advisory Board (2).

Separate lists of conclusions were drawn up by the Airframe and Structures Subgroup and by the Propulsion and Auxiliary Power Systems (APS) Subgroup. Representative of the panel's conclusions, however, is the following quotation from the report of the Power and APS Subgroup:

"It is the opinion of the subgroup that no entirely new fabrication method must be developed in order to manufacture the components of the future. The basic fabrication methods listed... are capable of fabricating existing and new materials into the required configurations. The principal needs... lie in developing established methods for new materials, especially the refractory metals, and in expanding the size capacities of processes to produce parts several times the size of existing components. In only one area, the fabrication of nonmetallic components, will any essentially new processes have to be developed and even these will utilize already developed pilot techniques."

Most critical areas in the manufacturing techniques categories were indicated to be joining and surface conditioning. Most critical material categories

are the refractory materials -- the refractory metals, the super alloys, and the ceramic materials.

Though the MAB report serves a useful function in delineating critical Air Force needs, it is essential that a certain amount of highly speculative effort be directed toward the ever narrowing gap between service environments and manufacturing environments. Such speculation ultimately must cope with such matters as trying to establish theoretical upper bounds for material properties and for the characteristics of processes aimed at inducing "failure," in some sense, in these materials. Thus, in a broader sense, the need for development of basically new fabrication methods is an ever present one.

This point of view is validated by considering the relation of the processing environment to the service environment.

Let Ω be the set of all possible environments to which a material can be subjected in either theory or practice. Let F be the set of environments which are capable of inducing "failure" in some sense detrimental to the mission which the material must fulfill, and let S be the set of environments which are incapable of inducing such failure. Then

$$\Omega = F \cup S \quad (1)$$

and

$$F \cap S = O \quad (2)$$

where O is the null or empty set, and $\cup$ and $\cap$ denote union and intersection respectively. Thus the two sets together comprise the whole environment space and contain no common elements. All fabricating environments must belong to the failure set F , whereas all service environments must belong to the set S .

Now it is evident that F (and hence S) depends both on the material and on its mission requirements. As materials are developed to meet more exacting mission requirements, $S \longrightarrow \Omega$ and $F \longrightarrow O$. Thus one is forced to seek more diligently for ways to fabricate materials as these materials

approach perfection. In the limit, the ultimate material capable of survival in all environments could not be processed by any means. Of course such a possibility can be viewed only in a relative sense. On a cosmic scale, one might well consider that we may wish eventually to send space probes into environments incapable of being duplicated terrestrially. Therefore, since F and S are disjoint sets, our ability to explore space must be limited to our ability to produce sufficiently severe failure environments on earth.

As previously noted, the cohesiveness of a solid must decrease as the energy density approaches the binding energy. Therefore, the set F is an increasing function of energy density and, as energy is supplied to the solid, one might expect a wider range of process possibilities. Evidently, then, manufacturing techniques can be based on the use of environmental conditions of greater severity than those likely to be encountered in use. For example, if a material is designed to withstand a temperature of 3000°F, then by exceeding this temperature one should be able to process the material. However, as temperatures and pressures increase in the service environment, it will become less practical to process materials by such obvious extensions of the service environment. Instead it will be essential to look for synergistic possibilities.

7. PROGRAM FOR NEXT PERIOD

During the next 6-month period the broad study of deformation processes and the study of direct deformation processes will be completed. The former will be reported separately because of its importance as a guide to manufacturing process research.

Feasibility studies of promising effects will continue with emphasis on the experiments outlined in the present report.

Process synthesis efforts will follow the concepts for cooperative mechanisms developed in this report.

APPENDIX A

ELECTROMAGNETIC FORCES AND ENERGY DENSITIES

A rational search for electromagnetic effects that can be utilized in manufacturing processes must be supported by the means for calculating the forces, stresses, and energy and power densities involved. The necessary theory is developed in this appendix from Maxwell's field equations, followed by a brief discussion of the problem of coupling fields to loads, the load representing the workpiece.

A-1 General Formulation of the Stress Tensor

The most general formulation of mechanical forces on matter due to electric and magnetic fields is derived from the classical theory of radiation pressure. The derivation follows Page's "Introduction to Theoretical Physics," but the equations are written in the MKS system. The basic classic equations of Maxwell are restated as follows:

$$\nabla \cdot \bar{D} = \rho \quad (1)$$

$$\nabla \cdot \bar{B} = 0 \quad (2)$$

$$\nabla \cdot \bar{E} = -\frac{\partial \rho}{\partial t} \quad (3)$$

$$\nabla \times \bar{H} = \rho \bar{U} + \frac{\partial \bar{D}}{\partial t} \quad (4)$$

The force acting on a differential volume of material is given by

$$\bar{F} = \rho \bar{E} + \rho \bar{U} \times \bar{B} \quad (5)$$

where the bar indicates a vector quantity, and

$\bar{D}$ = electric flux density, coulombs/m²

$\bar{E}$ = potential gradient, volts/m

$\bar{B}$ = magnetic flux density, webers/m²

$\bar{H}$ = magnetic field strength, amperes/m

$\bar{U}$ = velocity, m/sec

ρ = charge density, coulombs/m³

$\bar{F}$ = force intensity, newtons/m³

In homogeneous, isotropic media,

$$\bar{D} = \epsilon \bar{E} = \frac{10^{-9}}{36\pi} \bar{E} \epsilon_r \quad (6)$$

where ϵ_r = relative dielectric constant, and

$$\bar{B} = \mu \bar{H} = 4\pi \times 10^{-7} \mu_r \bar{H} \quad (7)$$

where μ_r = relative permeability.

If charge density and velocity are eliminated from Equation (5), and the force $\bar{F}$ is integrated over the volume of a piece of material, the total force $\bar{K}$ is given in terms of the electric and magnetic field strength and material properties. This classical theory, of course, considers continuous distributions of matter and charge density and assumes linear and isotropic material with constant ϵ_r and μ_r . Certain intermediate algebraic steps are omitted here since the derivation is given in numerous texts.

$$\bar{F} = \epsilon (\nabla \cdot \bar{E}) \bar{E} + \mu (\nabla \times \bar{H}) \times \bar{H} - \epsilon \mu \frac{\partial \bar{E}}{\partial t} \times \bar{H} \quad (8)$$

The force equation must now be made symmetric with respect to the electric and magnetic vectors. Multiplying Equation (2) by $\bar{H}$, and Equation (3) by $\bar{D}$ and then adding one obtains:

$$\mu(\nabla \cdot \vec{H})\vec{H} + \epsilon(\nabla \times \vec{E}) \times \vec{E} + \epsilon\mu \frac{\partial \vec{H}}{\partial t} \times \vec{E} = 0 \quad (9)$$

Then, adding Equations (8) and (9), and using the vector identity

$$(\nabla \cdot \vec{V})\vec{V} + (\nabla \times \vec{V}) \times \vec{V}$$

one obtains:

$$\begin{aligned} \vec{F} = & -\epsilon\mu \left[\frac{\partial \vec{E}}{\partial t} \times \vec{H} + \vec{E} \times \frac{\partial \vec{H}}{\partial t} \right] \\ & + \nabla \cdot (\epsilon \vec{E} \vec{E} + \mu \vec{H} \vec{H}) \\ & - \frac{1}{2} \nabla (\epsilon \vec{E} \cdot \vec{E} + \mu \vec{H} \cdot \vec{H}) \end{aligned} \quad (10)$$

The total force $\vec{K}$ on a finite volume of material is found by integrating $\vec{F}$ over the volume $\mathcal{V}$:

$$\begin{aligned} \vec{K} = \int_{\mathcal{V}} \vec{F} d\mathcal{V} = & -\epsilon\mu \frac{\partial}{\partial t} \int_{\mathcal{V}} \vec{E} \times \vec{H} d\mathcal{V} + \int_{\mathcal{V}} \nabla \cdot (\epsilon \vec{E} \vec{E} + \mu \vec{H} \vec{H}) d\mathcal{V} \\ & - \frac{1}{2} \int_{\mathcal{V}} \nabla (\epsilon \vec{E} \cdot \vec{E} + \mu \vec{H} \cdot \vec{H}) d\mathcal{V} \end{aligned} \quad (11)$$

The second and third integrals can be converted to surface integrals over the surface of volume $\mathcal{V}$ by well-known vector theorems:

$$\begin{aligned} \vec{K} = & -\epsilon\mu \frac{\partial}{\partial t} \int_{\mathcal{V}} \vec{E} \times \vec{H} d\mathcal{V} + \int_A (\epsilon \vec{E} \vec{E} + \mu \vec{H} \vec{H}) \cdot \vec{d}\vec{a} \\ & - \frac{1}{2} \int_A (\epsilon \vec{E} \cdot \vec{E} + \mu \vec{H} \cdot \vec{H}) \vec{d}\vec{a} \end{aligned} \quad (12)$$

The term $\vec{E} \times \vec{H}$ is the familiar Poynting vector, a surface power density. The volume integral gives a body force acting on the entire mass of volume V , and is, of course, determined by the value of Poynting vector inside the body. The surface integrals give forces acting on the outer surfaces of the body, and the values of $\vec{E}$ and $\vec{H}$ are those at the surface. It is important to determine the correct values of these vectors at each point. These surface forces are interpreted as arising from stresses acting on the surface A bounding V . To find the components of stress on a surface normal to the X axis, for example, one must evaluate the integrands with $d\vec{a} = \vec{i} dy dz$ thus obtaining:

$$X_x = \epsilon \left(E_x^2 - \frac{1}{2} E^2 \right) + \mu \left(H_x^2 - \frac{1}{2} H^2 \right)$$

$$Y_x = \epsilon E_x E_y + \mu H_x H_y$$

$$Z_x = \epsilon E_x E_z + \mu H_x H_z$$

Here, X_x is a normal stress, Y_x and Z_x are shear stresses acting on the YZ surface, and $E^2 = E_x^2 + E_y^2 + E_z^2$. The stress components on the surfaces normal to the Y and Z axis are similarly obtained.

The stress dyadic ψ is defined by

$$d\vec{K} = \psi \cdot d\vec{a} \quad (13)$$

where in rectangular coordinates

$$d\vec{a} = \vec{i} dy dz + \vec{j} dz dx + \vec{k} dx dy$$

The expanded stress dyadic is given by

$$\begin{aligned}
\psi = & \bar{i}\bar{l} \left\{ \frac{\epsilon}{2} (E_x^2 - E_y^2 - E_z^2) + \frac{\mu}{2} (H_x^2 - H_y^2 - H_z^2) \right\} \\
& + \bar{i}\bar{j} \left\{ \epsilon E_x E_y + \mu H_x H_y \right\} + \bar{i}\bar{k} \left\{ \epsilon E_x E_z + \mu H_x H_z \right\} \\
& + \bar{j}\bar{l} \left\{ \epsilon E_y E_x + \mu H_y H_x \right\} + \bar{j}\bar{i} \left\{ \frac{\epsilon}{2} (E_y^2 - E_z^2 - E_x^2) + \frac{\mu}{2} (H_y^2 - H_z^2 - H_x^2) \right\} \\
& + \bar{j}\bar{k} \left\{ \epsilon E_y E_z + \mu H_y H_z \right\} + \bar{k}\bar{i} \left\{ \epsilon E_z E_x + \mu H_z H_x \right\} \\
& + \bar{k}\bar{j} \left\{ \epsilon E_z E_y + \mu H_z H_y \right\} + \bar{k}\bar{k} \left\{ \frac{\epsilon}{2} (E_z^2 - E_x^2 - E_y^2) + \frac{\mu}{2} (H_z^2 - H_x^2 - H_y^2) \right\}
\end{aligned} \tag{14}$$

This dyadic is symmetrical. It expresses in the most general form the surface forces on homogeneous, isotropic matter that are due to electric and magnetic fields. If a constant electric (or magnetic) field is applied, the H (or E) terms are zero.

As an example, consider a one-centimeter cube of material of relative dielectric constant $\epsilon_r = 4$ and relative permeability $\mu_r = 1$, aligned with its edges along the principal axes, rigidly supported at one YZ face, subjected to a steady electric field in the X direction, and immersed in free space. Then

$$\psi = \bar{i}\bar{i} \frac{\epsilon}{2} E_x^2 - \bar{j}\bar{j} \frac{\epsilon}{2} E_x^2 - \bar{k}\bar{k} \frac{\epsilon}{2} E_x^2$$

$$d\bar{K} = \bar{i} \frac{\epsilon}{2} \int E_x^2 dy dz - \bar{j} \frac{\epsilon}{2} \int E_x^2 dx dz - \bar{k} \frac{\epsilon}{2} \int E_x^2 dx dy$$

$$K_x = \frac{\epsilon}{2} E_x^2 \times 10^{-4}; \quad K_y = -\frac{\epsilon}{2} E_x^2 \times 10^{-4}; \quad K_z = -\frac{\epsilon}{2} E_x^2 \times 10^{-4}$$

The material is compressed in the X direction by the normal force K_x . Similarly, K_y and K_z tend to stretch the material in the Y and Z directions. The effective value of E_x is the difference between the values outside and inside the body. If the free space field is of strength $\bar{E}$, then $E_x = \frac{\epsilon_r - 1}{\epsilon_r} \bar{E}$.

Assuming a gradient, $\bar{E} = 10^5$ volts/cm, the stress K_x in the direction is

$$K_x = \frac{\epsilon}{2} E_x^2 \times 10^{-4} = \frac{10^{-9} \times 4}{72\pi} \left(\frac{4-1}{4}\right)^2 (10^5)^2 \times 10^{-4} = 0.1 \text{ newton/cm}^2 \\ = 0.145 \text{ pound/in.}^2$$

Obviously, presently attainable electrostriction forces are small.

To illustrate magnetic forces, assume a steel body of $\mu_r = 1000$, subjected to a field of $2 \cdot 10^4$ gauss, or 2 webers/m². The resulting differential K_x is approximately 1.6×10^3 amp/m. The tension stress is then

$$K_x = \frac{\mu}{2} H_x^2 \times 10^{-4} = \frac{4\pi \times 10^{-4}}{2} (1.6 \times 10^3)^2 = 1,600 \text{ newtons/cm}^2 \\ = 2,320 \text{ pounds/in.}^2$$

Since it is the difference in field strengths at the outer and inner sides of a surface which determines the net force, it would seem that static electric fields are effective only on dielectric materials, and static magnetic fields only on ferromagnetic materials. When electromagnetic waves are used, the reflection and transmission effects at the surface will result in a differential field strength, even if high permeability materials are not present.

A-2 Forces on Current-Carrying Conductors

Magnetic force on material may be applied by passing heavy currents through the work piece. The resulting heat effects might at the same time lower the yield point. The differential equation characterizing this effect is:

$$\vec{F} = \vec{J} \times \vec{B} \quad (15)$$

where $\vec{F}$ = force per unit volume, newtons/m³

$\vec{J}$ = current density, amperes/m²

$\vec{B}$ = flux density, webers/m²

$\vec{B}$ is the actual flux density at the point where $\vec{J}$ exists, and is, of course, the resultant of the impressed magnetic field and the magnetizing effect of the current in the work piece. To illustrate this effect, assume a current density of 1000 amperes/in.² flowing through a metal bar located with its length normal to a resultant field of 100,000 gauss. Then,

$$J = \frac{1000}{(2.54)^2} \times 10^4 = 1.55 \times 10^6 \text{ amp/m}^2$$

$$B = 10^5 \times 10^{-8} \times 10^4 = 10 \text{ webers/m}^2$$

$$\vec{F} = 1.55 \times 10^7 \text{ newtons/m}^3 = 57 \text{ pounds/in.}^3$$

If the bar were unrestrained and had a cross section of one square inch, it would be uniformly loaded with 57 pounds/inch. Selective nonuniform loading could be accomplished, within limits, by properly shaping the current distribution and the magnetic field. As in all cases of electromagnetic force production, a difficult problem of field and material geometry is presented. The difficulty with fields is that they do not have sharp boundaries; they "smear out" into continuous distributions. Sometimes these problems can be readily solved by analog methods.

A-3 Volume Energy Densities

The volume energy densities in joules/m³ are given by

$$\begin{aligned}W_E &= \frac{\epsilon}{2} E^2 \\W_M &= \frac{\mu}{2} H^2 = \frac{1}{2\mu} B^2\end{aligned}\tag{16}$$

where E = volts/m

B = webers/m²

For $E = 10^5$ volts/cm.:

$$\begin{aligned}W_E &= \frac{\epsilon_r}{72\pi} \times 10^{-9} \times (10^7)^2 = 442 \epsilon_r \text{ joules/m}^2 \\&= 4.42 \epsilon_r \times 10^{-4} \text{ joules/cm}^3\end{aligned}$$

For $B = 10^5$ gauss:

$$\begin{aligned}W_M &= \frac{10^5 \times 10^{-8}}{8\pi \times 10^{-7} \mu_r} \times 10^4 = \frac{3.79}{\mu_r} \times 10^6 \text{ joules/m}^3 \\&= \frac{3.79}{\mu_r} \text{ joules/cm}^3\end{aligned}$$

One joule is 0.738 foot-pound.

High electric-field strength causes ionization and disruption of matter. At normal atmospheric conditions dielectric-breakdown-voltage gradients range from 3×10^6 volts per meter for air to 4×10^7 volts per meter for thin sheets of high quality siliconic rubber. This dielectric strength limits the possible field volume energy densities. No such disruptive effect is known in magnetic fields. Realizable energy densities are much higher in magnetic than in electric fields.

Note: The foregoing discussion applies to static or non-time-varying fields. In electromagnetic waves there is a fixed ratio of E to H , which causes the energy to be equally divided between the E and H fields. The energy is propagated in the direction of the wave and is not stored as it is in a capacitor or a magnet.

A-4 Means to Obtain Power Densities

The rate at which energy can be liberated or transformed is as important as the storage density. Achievable power densities depend on the mechanism by which energy is supplied to the load.

High-frequency electromagnetic energy might be applied by apparatus like a pulsed radar. As an example of the present state of the art, a peak power of 250 megawatts can be supplied in pulses of 0.25 microsecond with rise and fall times of 30 nanoseconds. One such pulse supplies about 60 joules.

A common method of supplying energy pulses is by the discharge of capacitor banks. The resulting power is a function of time and varies widely with the electrical parameters of the circuit. Since all circuits possess resistance, inductance and capacitance, the current is always of the form:

$$i = \frac{E_0}{R(\gamma - \alpha)} \left[\alpha \left(\alpha - \frac{1}{L} \right) e^{-\alpha t} - \gamma \left(\gamma - \frac{1}{L} \right) e^{-\gamma t} \right]$$

where

$$\alpha = \frac{R}{2L} + \sqrt{\left(\frac{R}{2L} \right)^2 - \frac{1}{4LC}}$$

$$\gamma = \frac{R}{2L} - \sqrt{\left(\frac{R}{2L} \right)^2 - \frac{1}{4LC}}$$

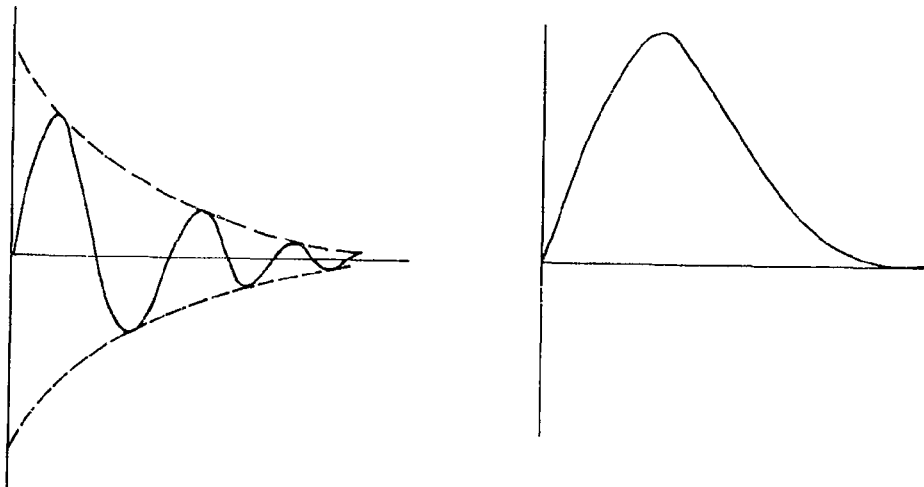
R = total resistance,

C = capacitance

L = inductance

E_0 = initial potential across the capacitor

The current is either oscillatory or forms one pulse, viz:



The total energy, $CE_o^2/2$ is converted to heat in the resistance, only a part of which represents the useful load. The peak power available is something less than E_o^2/R and decays exponentially with a time constant equal to $RC/2$. Circuits for applying energy by capacitor discharge should be carefully designed for the specific load, whose electrical characteristics must be accurately known.

When a spark gap is used as a switch to close the discharge circuit, some of the energy is lost in the spark. More sophisticated switches of better efficiency may be used, however.

One microfarad stores $1/2$ joule per (kilovolt)², substantially all of which can be liberated in a few microseconds, provided the inductance of the circuit can be kept very small.

As an example of capacitor-discharge metal forming, current research at Republic Aviation Corporation may be cited (16). It is reported that the resistance changes in a complicated way during the discharge so that the decrement factor

does not remain constant. Simple exponential decay therefore does not describe the discharge. Maximum power at the spark gap is developed when the circuit parameters are so chosen that the circuit is critically damped in the sense that the resistance is adjusted to just prevent oscillation. A typical discharge reported in the study is 9720 joules at 9000 volts. With critical damping, 81.5 percent of the energy is delivered to the load. A vacuum switch is used to initiate the discharge. An initiating wire is placed in the discharge gap, the diameter of which is chosen to obtain the critically damped condition. The inductance, capacitance and the resistance of the circuit external to the gap remain practically constant. Typical values are 240 microfarads, 50×10^{-8} henry, 0.003 ohm in permanent circuit structure, and 0.15 ohm in the initiating wire. The installation is designed for a maximum energy storage of 155,000 joules (960 microfarads at 18,000 volts).

A-5 Methods of Coupling to the Load

Some of the coupling factors have already been mentioned briefly. The forces due to electric, magnetic and a-c electromagnetic fields depend on a difference in field strength between the outer and inner sides of the surfaces. These differences, in turn, depend on differences in resistivity, permeability and permittivity between the material of the work piece and the ambient matter. The relative values of sample dimension and the wave length of the radiation also are important. In the case of the dielectric bodies, the material used to support the work piece may also be important. It is conceivable that tuning of r-f fields could increase the forces by establishing standing waves when the work piece is backed by suitable reflecting surfaces.

It is evident that especially shaped force-field configurations can be established in work pieces by properly shaping the electrodes, coils, or antennas which produce the fields. Such shaping is commonly done in induction heating, and a large amount of design information has been accumulated. The mathematical problem would always be difficult, but theory could be used as a guide to empirical solutions. It must be remembered that true discontinuities in fields are practically nonexistent.

When forces act on electric currents flowing in metal work pieces, both the external magnetic and the internal current-flow field can be shaped to develop forces in preferred directions. The current pattern can be controlled within limits by the shape of the work piece and the lead-in connections, and perhaps also by local heating to alter resistivity. It should be noted that if the magnetic field and the current are ac of the same frequency and properly phased, the forces will be unidirectional. Conceivably, the currents could be established by induction. As an example, consider a steel plate with a round hole in it, this hole to be flanged or dimpled. By applying ac magnetic flux through the hole, circumferential currents would be induced in the steel. The radial forces developed would tend to enlarge the hole, and because of local softening due to heat, the desired deformation might occur. By use of an external coil, this idea has been used for swaging tubes to a reduced diameter. An ac magnetic field induces currents in the work piece, which acts like the short-circuited secondary of a transformer. It is of course necessary to have values of parameters which result in a reasonably good power factor or phase-angle difference.

When steady electric or magnetic fields are involved, the field in a region of constant properties is computed by means of the LaPlace equation if the boundary values are known:

$$\nabla^2 \phi = 0 \quad (17)$$

where $\bar{E} = -\nabla \phi$

and $\bar{E} =$ field strength.

The values of the potential ϕ on certain bounding surfaces are established independently by some method of control. In practical cases, the properties of the matter in the field will not be constant but will vary from point to point. This variation is described by means of a flux density function, related to the field strength, viz:

$$\bar{D} = \epsilon \bar{E}$$

For amorphous and polycrystalline materials, ϵ can generally be treated as a scalar constant, but $\bar{D}$ is sometimes a nonlinear function of $\bar{E}$. Single crystals frequently are anisotropic, and ϵ may become a dyadic.

The flux density is related to the source distribution by an integral:

$$\int_A \bar{D} \cdot d\bar{a} = \int_V \rho dv$$

where ρ = source density and the potential function is related to the source function by the integral:

$$\Phi = \frac{1}{4\pi\epsilon} \int \frac{\rho}{r} dv$$

where r = distance from dv to the point at which the potential is determined. The above equations are written for electric fields, but magnetic fields are governed by the same equations.

When the field strength varies harmonically with time, the relationships are much more involved, because of the interrelation between the electric and magnetic fields, Equations (3) and (4). High-frequency fields also exhibit the further complications of finite propagation velocity and time delay, causing energy to be radiated.

Formal solutions are possible only for the most simple geometry. Digital computer solutions of boundary value problems are very time-consuming. Analog methods are frequently very helpful, particularly for two-dimensional topologies. Engineering techniques for designing equipment to shape fields to specified shapes have not been highly developed as yet, except for radiating antennas and induction heating coils, chiefly because engineering applications of shaped fields are few.

APPENDIX B

ELECTRON, ION AND LASER BEAM PROCESSES

The material removal and material addition capabilities of electron, ion, and laser beams are discussed and compared in this appendix. Each energy form is discussed in turn for the two use categories, the better-explored electron beam serving as a basis for comparison. The outline of an experiment for investigating the interaction mechanism between a laser beam and engineering materials is included.

B-1 Material Removal

B-1.1 Electron Beams

Electron beams can machine literally any material. However, drilling and milling operations employing electron beams are not yet widely in use, apparently because characteristic burrs (of micron size on the edges of cuts) are objectionable. These burrs are formed when a portion of molten material lining the cavity is blown out by the internal vapor pressure of the melt, and some of the material condenses on the edge of the cut.

The procedure used to drill a hole or mill a slot is to apply power in short pulses in such a manner that the successive layers of the work piece are evaporated without adversely affecting adjacent material.¹ In tungsten, for example, K.H. Steigerwald (17) found that it takes 10^{-8} seconds for the energy of a 100-kev electron beam at 10^9 watts/cm² to be absorbed in the impacted surface layer and raise its temperature to the melting point. Calculating the heat conducted away from this layer, it is found that it takes 10^{-5} seconds for a point which is 0.0003 inches away to reach melting temperature and 7×10^{-6} seconds for a point only 0.00004 inches away to do so.

¹See Appendix C for a discussion of the interaction mechanism between electron beams and matter.

Either of these times is greater by a factor of 10^3 than the melting time under the beam. From this example, it is seen that there is ample time to vaporize the intended layer of material without melting adjacent material only a few mils away.

The minimum width slot or minimum diameter hole which can be produced is a function not only of the beam spot size but also of the depth of the slot or hole. For depths greater than about 0.020 inch, energy is absorbed by the walls, and the hole diameter will increase to approximately twice the beam diameter. With workpieces much less than 0.020-inch thick, just the reverse is true. As the thickness of the material approaches the penetration depth of electrons in that material, the less dense outer edge of a nonuniform beam tends to pass through the workpiece without transferring sufficient energy to evaporate it. The center of the beam is much "hotter" however and does cause evaporation of the material. Thus, the hole produced by an electron beam can be smaller in diameter than the beam itself. For example, under optimum conditions, a 0.0008-inch diameter beam can produce a hole only 0.0004 inch in diameter (18). The deepest straight hole or slot that can be machined in metals is about 0.08 inch. Beyond that depth, the walls absorb the beam energy, and side-wall taper becomes appreciable.

The instantaneous intensity of the beam, and its focus, shape and position can be controlled accurately. Since the cutting energy is pulsed (from 1-5000 cps), electron-beam machining operations are easily adapted to programming by controlling the pulsing with a scanner. A unit which can follow intricate patterns by this method has been developed.

The two strong points of material removal with electron beams are:

1. The technique is applicable to any material. It has been used to put holes in glass, diamonds, and nearly the full range of metals.

2. It will drill holes less than 0.0008 inch in diameter.

The limitations are:

1. Cut depths are usually less than 0.080 inch.
2. Holes are usually not "clean" --- the edges of the cuts and the bottom have micron-size burrs.

Unexploited potential in electron-beam machining may be found in the effects caused by special environmental gasses. Some progress in this area has already been reported (19).

B-1.2 Ion Beams

Ion beams offer several advantages over electron beams for material removal. For example, because the ion beam sputters material off the workpiece instead of vaporizing it off, heat conduction is not a problem, and the machining operation could operate continuously as opposed to pulsed operation. Moreover, sputtering ratios at potentials of about 15 kv indicate the possibility of macroscopic as well as microscopic machining operations. Again, as in electron beam machining, the greatest obstacle to actual achievement of macroscopic ion-beam machining is the inability of available ion-beam devices to generate a beam of sufficient power.

Earlier preliminary computations (20) gave yield figures that were about the same as those presently achieved in electro-chemical milling processes. Moreover, the ion beam would have the ability to machine nonconductors such as ceramics, and the control which the operator would have over the beam would be inherently better.

B-1.3 Laser Beam

The mechanism by which a laser beam removes material is quite similar to that of the electron beam. Both vaporize the material by generating

intense heat within the target area. However, a laser beam can expose the target area to higher energy densities for shorter periods of time than an electron beam. A further distinct advantage of the laser beam over electron beams in the processing of thin films was recently pointed out (21). Because of the high acceleration voltages (up to 150 kv) needed for small spot size, the electron beam will penetrate the first surface layers and cause sub-surface heating, resulting in ruptures at the surface and irregular definition of the lines cut. Light beams would have no such effect due to their extremely shallow ($\sim 500 \text{ \AA}$) penetration depth.

At the present time, the laser can drill holes from .001 to .010 inch in diameter in thin sheets of any material. It has been noted that there is practically no oxidation along the walls of the machined areas regardless of the atmosphere. The actual mechanism by which a laser beam drills a hole is unknown.

An experiment for studying the interaction mechanism between a ruby laser beam and engineering materials has been formulated and will be performed during the next contract period. The shape and durability of the light pulse from the optical maser will be varied by control of the pulsing circuit parameters and by delaying the onset of stimulated emission. The latter can be accomplished through the interposition of a rotating shutter between the ruby and a separated end reflector. The relations between the parameters of the optical maser pulse, material removal rate, and configuration control will be studied.

B-2 Material Addition

B-2.1 Electron Beams

Electron beams serve two different material-addition technologies. These are welding, in the conventional sense, and evaporation. They are discussed separately below.

B-2. 1. 1 Welding

In welding, electron beams have contributed to an "order of magnitude" increase in the state of the art. The characteristics of electron beams permit the design of extremely versatile welding equipment. A single high-voltage machine can weld micromodule electronic circuits as well as two-inch thick slabs of stainless steel. The only limitation on workpiece size is the size of the work chamber.

In addition to the versatility of the electron beam welder, the welds it produces are unique. First, there is virtually no weld contamination problem, and the formation of harmful intermetallic phases is kept at a minimum. Second, weld depth-to-width ratios as high as 40 can be achieved compared with about unity ratio for other fusion techniques. Third, the metal adjacent to the weld suffers very little distortion and thermal influences on its microstructure are reduced because there is much less molten metal to give off heat. Lastly, welds can be obtained between materials which were thought "unweldable" previously. Some of the difficult-to-weld materials which have been joined by electron beams are copper to zircoloy, stainless steel to niobium, tempered stainless steel to tempered stainless steel, molybdenum to alumina, tungsten to alumina, niobium to alumina, beryllium to beryllium, and alumina to alumina.¹

Microweldments produced by electron beams on microminiature electronic components are also characterized by excellent mechanical and metallurgical properties, and provide a high degree of structural reliability. Electron beams offer a solution to one of the most vexing problems in thin-film circuitry, that of joining leads to thin films without destroying the film in the process.

¹Private Communication from Hamilton Standard, Division of United Aircraft Corporation, Windsor Locks, Connecticut.

In summary, the advantages of electron beam welding are:

1. Extreme versatility
2. No weldment contamination
3. High depth-to-width ratio
4. Low distortion
5. Small heat-affected zone
6. Ability to weld refractory materials
7. Amenable to precise control.

The work-chamber restrictions may not be present much longer as a result of some successful experimentation with electron-beam welding in an inert gas environment(23).

B-2.1.2 Evaporation

Electron beams can be used in practically every aspect of thin-film circuit production. For example, an electron beam can provide the energy for the following operations:

1. Initial evaporation and deposition
2. Subsequent milling required on resistive elements
3. Annealing or alloying of selected portions
4. Final attachment of lead wires.

Each of these operations when performed by an electron beam has certain distinct advantages over more conventional procedures. Conventional evaporation is limited to materials whose melting point is less than 1000°C due to crucible contamination or reaction. Electron-beam evaporation allows the use of water-cooled copper crucibles and provides the necessary power density to evaporate metals like tungsten and tantalum. (Previously, thin films of tungsten or tantalum were obtained through sputtering.)

Milling the resistive elements with electron beams instead of using etching techniques circumvents the necessity of providing masks and allows for constant monitoring of the component during the milling operation.

Annealing or alloying of selected portions of the thin-film circuit can be accomplished without adversely affecting neighboring areas through the close control and small spot size associated with electron beam devices. These characteristics also make the electron beam an ideal tool for attaching the lead-wires to the appropriate thin film circuit areas. Because of these unique characteristics, electron beam production facilities now available (24) can produce 80 to 500 thin-film microcircuits in a two-hour cycle, as opposed to about one per hour with conventional equipment.

A possible extension of electron beam application in the field of microcircuitry involves the direct fabrication of electronic circuits from the raw materials with a minimum of nonfunctional elements. Such a circuit would have its elements, both active and passive, built up in successive layers deposited by evaporation of different materials to carry out the necessary electronic functions. The entire operation plus the connecting of lead wire could be accomplished by means of electron beams.

It is anticipated that further applications of electron beams which fall within the category of production tools will be along the lines presently being exploited. The development of production facilities which can make use of electron beams in each of the applications mentioned is being carried out at a rapid pace. Improvements and refinements of these processes will come as a matter of course, but it is advisable to provide guidance of such efforts on the basis of improved understanding of process characteristics and the type of systems approach developed here.

B-2.2 Ion Beams

Ion beams offer promise in another phase of material addition, that of composite materials. Since at low energies (< 1 kv) ions incident on a target have insufficient energy to sputter and instead form a deposit, they

offer a means by which surface layers of a desired composition could be formed on a material. These surface layers could be such as to retard oxidation, lower vapor pressure, or change the reflection coefficient for a particular frequency of optical or infrared radiation.* The possibility of precise control of the ion beam also makes it a candidate for use in the thin-film industry. For example, the deposition of thin-film circuits would be possible without going through a laborious masking process.

B-2.3 Laser Beams

Laser beams can contribute significantly to the welding phase of material addition. As was mentioned earlier, laser beams are very similar in their interaction with materials as electron beams. However, at the present time, laser-beam welding is limited to welding thin sheets ($\sim .005$ in.) of materials on a pulse or spot-welding basis. Overlapping pulse welds can, of course, be substituted in place of a continuous weld. The most significant aspects of laser-beam welding which makes it especially attractive involves the low oxidation of the laser weld due to the short pulse duration and the extreme degree of control coupled with the very small spot size attainable without the limitations imposed by artificial atmospheres or physical contact with the workpiece.

Just from those characteristics mentioned above, it is clear that the laser can be a valuable production welding tool especially adaptable to mass production and/or automated techniques.

* Surface modification by ion beams is discussed in more detail in Appendix D.

APPENDIX C

PENETRATION DEPTH AND POWER DENSITIES OF ELECTRON BEAMS

The theoretical penetration depth of electrons in metals is 0.003 inch. Yet, welds in one-inch-thick materials have been produced! In this appendix we examine the apparent paradox by physical reasoning and calculations of energy relations from published welding data. Achievable power densities are then discussed.

The electron beam is essentially a heat-producing tool capable of being focused and controlled to a high degree. The heating is the result of an almost 100 percent energy transfer between the electrons making up the beam and the target material. The dominant mechanism by which the energy transfer takes place is the same for all materials, namely that when high-velocity electrons impinge upon a material, they suffer collisions and, in the process, give up their kinetic energy to the material. Because of the large difference in their masses (a factor of 10^4), the electrons cannot transfer their kinetic energy directly to the lattice atoms of the material (25). Rather, this energy is transferred to the lattice electrons which then contribute to the vibrational energy of the lattice. Thus, the amplitude of the lattice vibrations is increased and an almost instantaneous temperature rise within the target area results. Furthermore, since the electron penetration depth in metals is only about .003 inch, all of the energy transferred to the material is localized within the target area, and losses are essentially limited to thermal conduction from the target area. Indeed, it is this specific property of electron beams which enables them to perform many of their unique functions. Because of the combined high power density of the beam, the shallow penetration depth, and the low thermal losses from the target area, the energy density within the target area very quickly approaches the theoretical binding energy of the material.

Another result of the shallow penetration depths is the narrow heat-affected zones characteristic of electron beam welds. Consider an electron

penetration depth an order of magnitude greater than the classical limit for iron (0.003 inch)! Then with a 0.010-inch diameter electron beam incident upon the material, we would expect to find a tear-drop-shaped, heat-affected zone immediately under the beam. This tear-drop shape is a result of Rutherford-type scattering of the electrons by the lattice-electrons of the target material. If we assume only small angle scatter, $\sim 5^\circ$ per collision, and 10 collisions per incident electron, at a penetration depth of 0.030 inch, then the mean horizontal displacement of the electrons would be about 0.010 inch. Thus for a 0.010-inch diameter beam, the minimum width of the heat-affected zone would be 0.030 inch, neglecting thermal conduction. This figure would also correspond to the minimum diameter hole which could be drilled in materials substantially thicker than the electron penetration depth. Actually, the electron penetration depth is 0.003 inch for iron, and the mean horizontal displacement of the electrons is only about 0.001 inch; therefore a 0.010-inch diameter beam theoretically produces a heat-affected zone of 0.012 inch. Weld widths in stainless steel of less than 0.030 inch have been reported (26). Thus, it would seem that the narrow heat-affected zones in weldments can be explained by adherence to "classical" electron penetration depths.

The question then arises why electron beams can make welds with depth up to one inch although the penetration depths are three orders of magnitude less. To explore this paradox, the energy available in the electron beam and the energy required to vaporize a given volume of material corresponding to the weld cavity were compared (Figure C-1).

In our analysis we computed the energy required to vaporize a volume of material (V_0) equal to the cross section of the electron beam times weld depth and compared this energy with E_0 , the energy actually expended in producing the weld (27). The diameter of the electron beam was given to be 0.010 inch.

For most welding speeds the actual energy expended was available only for one material thickness (27). However, it is known from other investigations (26) that, for a given welding speed, depth of penetration is directly

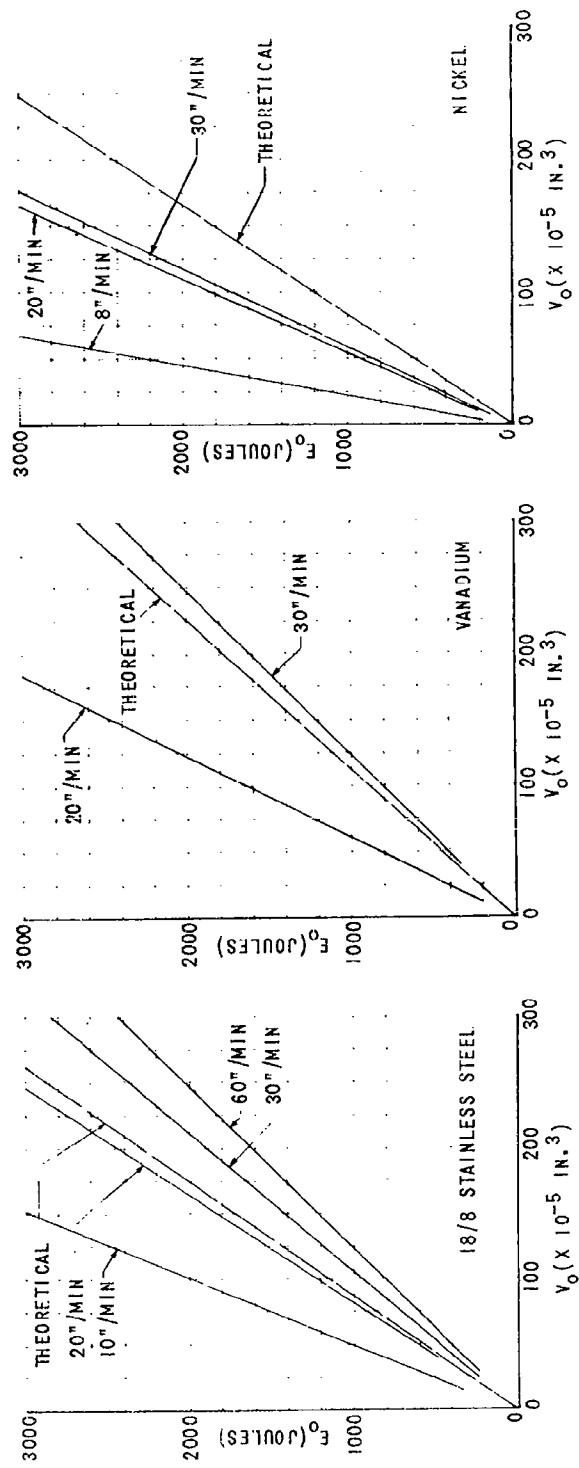
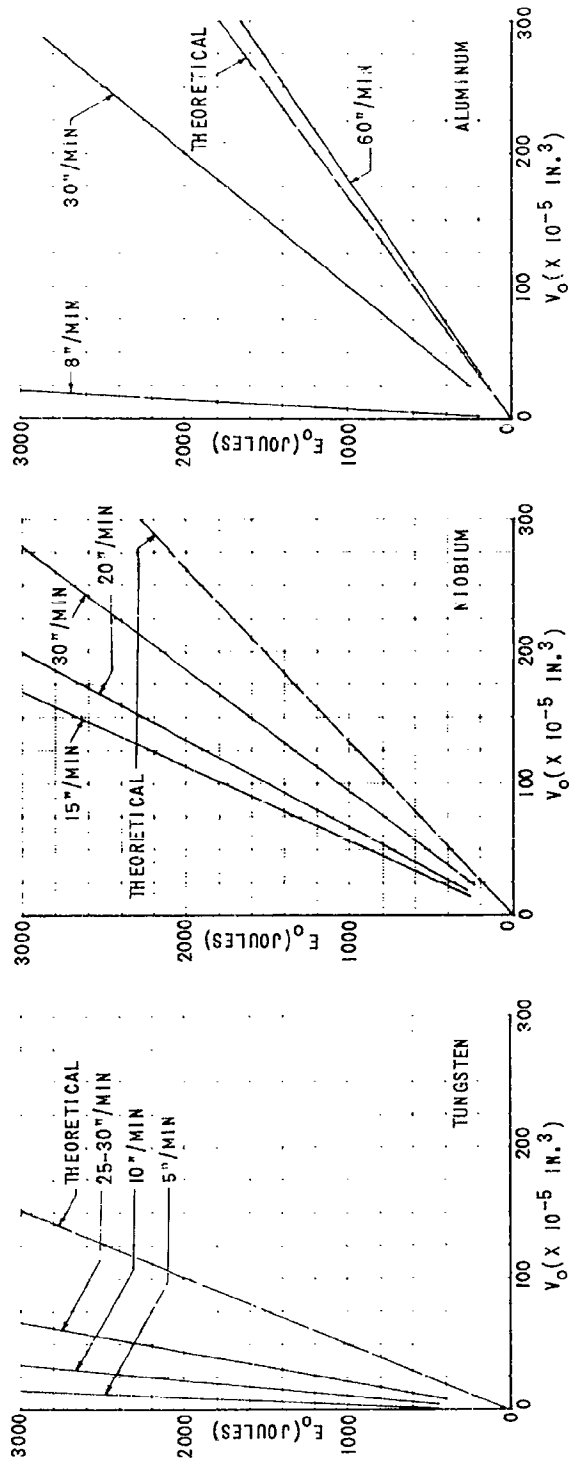


Figure C-1 ENERGY VERSUS VOLUME RELATIONSHIP AT VARIOUS WELDING SPEEDS



C-4

Figure C-1 (Cont.) ENERGY VERSUS VOLUME RELATIONSHIP AT VARIOUS WELDING SPEEDS

NM-1559-P-3

proportional to beam power. Therefore, the $E_o - V_o$ curves were plotted as straight lines. It can be seen from the graphs that, for the higher welding speeds, the slope of the actual $E_o - V_o$ curve is greater than the slope of the theoretical curve. For lower welding speeds, the trend is reversed. An accurate energy balance to account for the losses has not been calculated.

The fact that less than vaporization energy was expended in producing a weld cavity at high welding speeds supports the view that a significant portion of the material displaced from the cavity must be ejected in molten form. The ejection is probably brought about by the vaporization of sub-surface areas in a manner described by Schwartz in Reference (25). His explanation is supported by the fact that in observing an electron-beam welding process, it can be seen that there is a continuous stream of metal droplets thrown out from the weld cavity to a height of several inches above the weld. (It would be an interesting experiment to measure the amount of material ejected for a given series of welds in an attempt to account for the total energy expended.) A second explanation given for the ejection process requires the vapor stream from the bottom of the cavity to drag with it portions of the molten material lining the cavity. However, this view would require complete vaporization of the cavity volume.

From graphs similar to those presented, it is possible to predict the approximate power necessary to produce a given weld at a given speed for specific materials. It should be noted here, that the spot size produced by the beam is an important parameter since it determines the power density delivered by the beam. On small spot areas (say 0.0001 square inch, power densities exceeding those of the electric arc by a factor of 10^4 can be achieved. A change in spot size for the same total power delivered can result in entirely different welding characteristics. The power density has been calculated by Schwartz (25) for an optimum optical system as:

$$D = 4 \frac{IV}{\pi d^2} \quad (1)$$

where D = power density
 i = beam current
 V = beam voltage
 d = beam spot diameter

Since $d \propto \left(\frac{i}{V}\right)^{3/8}$ the spot diameter can be eliminated from (1), and

$$D \propto i^{1/4} V^{1/4} \quad (2)$$

The proportional relation (2) demonstrates that high-voltage electron beams have inherently greater power density than low-voltage beams at the same power level.

If the beam current exceeds that necessary for creating a "pinch," then relation (2) no longer applies. The possibility of producing much higher power densities is being investigated by Prof. W.H. Bennett, North Carolina State College, a consultant to the project. Under a Navy contract,¹ he is building a device that is to produce 5-kw electron beams using space-charge neutralization to focus the beam and the pinch effect to confine and stabilize it. Success of the endeavor would allow a significant increase in the range of electron-beam welding and cutting applications.

¹Contract No. Nonr 486-10.

APPENDIX D

SURFACE MODIFICATION BY ION BEAMS

The modification of material surfaces so as to extend or change the properties of the bulk material is important to the concept of "made to order" material properties (2). Although various surface modifications, such as shot-peen hardening, have been practiced for many years, the full potential of this concept has not been realized. The direct injection of dislocations via ion beams is proposedly a means for surface modification.

High energy sputtering experiments at Oak Ridge National Laboratory (28) indicate that at ion energies of 50 kev and above, the collision cross-section of material-ion systems decreases, and penetration becomes the dominant interaction mechanism. In other words, if the energy of the ion beam is sufficient, the incident ions will be infused into the surface layer of the target material. This infusion is tantamount to creating point defects (vacancies and interstitial host atoms) in a material, thus determining to a large degree the mechanical properties of that material. In consequence, high-energy ion beams have the potential for bringing about gross changes in the properties of the surface layer of materials. A point-defect-producing ion beam could contribute substantially to hardening, embrittlement, and oxidation retardation. A discussion of its potential in each of these areas follows.

D-1 Hardening

The surface hardening processes are solid solution, transformation, and work hardening. The general principle of each of these hardening methods is to produce misfits in the microstructure of the materials, thereby impeding the progress of dislocations and slip planes. Solid solution hardening produces a misfit by introducing foreign atoms in the host lattice either substitutionally or interstitially. Transformation hardening involves the formation of stable compounds or polymorphic forms within the host material (e.g., the martensitic steels). Work hardening is essentially the introduction of dislocations

to prevent or impede "micro-slip" (microscopic dislocation movement). Each of the three hardening processes is time consuming and likely to produce warping and size change in treated parts.

The ion beam has the potential of duplicating the results of each of the hardening methods without undesirable side effects, and of adding unique features of its own. For example, if the bombarding ion is within about 15 percent of the size of the host ion, substitutional solid solutions may form. However, at low temperatures and short periods of time (relative to those required for diffusion) the displaced host ion would have to take up a nearby interstitial position. Since the host ions are large compared with the usual interstitials, there would result an increase in volume of surface layer of material. Thus, in addition to the hardening effect of the foreign substitutional ions, there is an over-all compressive stress within the surface layer similar to that encountered in shot-peening.

If the bombarding ions are small compared to the host ions ($\sim \frac{1}{2}$), interstitial solid solutions will result with very little over-all stress incurred. This situation should result in a minimum "hardness per incident ion" which can be obtained with ion beams. Even this least efficient hardening process via ion beams has interesting features. For example, Ogden and Jaffee (29) report that the Vickers Hardness of iodide titanium may be raised from 60 to 280 by the addition of 0.5 wt. percent of oxygen equivalents. (An oxygen equivalent is that amount of carbon or nitrogen which has hardening properties equal to the addition of 1% oxygen: $2/3\%$ carbon $\equiv$ 2% nitrogen $\equiv$ 1% oxygen.) If one wished to accomplish such a hardening operation on one square centimeter of surface layer and affect a depth of about 1000 atomic layers, the addition of approximately 3×10^{18} oxygen ions would be required (30). The energy necessary to penetrate aluminum to a depth of 8000 angstroms (or 2000 atomic layers) with nitrogen was 500 kev in a recently reported experiment (31). At the present time, ion-beam generators can produce current densities of about $.5 \text{ amp/cm}^2$ which represents close to 1.5×10^{18} ions/sec. Thus, this hypothetical hardening operation would take about two seconds to complete. Vaughan et al. (32), report the following relationships between oxygen content and Knoop hardness index for tantalum. The hardening times are for the conditions described above.

<u>Oxygen Content</u>	<u>Knoop Hardness</u>	<u>Ion-Beam Hardening Time</u>
0.11	122	1/2 sec.
1.02	216	4 sec.
3.16	534	12 sec.

One of the more interesting facets of ion-beam hardening lies in the possibility of producing both substitutional and interstitial solid solutions of compositions which do not exist under the near-equilibrium conditions of conventional metallurgy. (Unless excessive heating accompanies ion impregnation, equilibrium solubility restrictions are not expected to interfere.) Therefore, ion-beam impregnation would be a possible means of creating new materials.

Apart from solid-solution hardening, ion beams offer possibilities for hardening by bombarding with ions which form stable compounds with the base metal (such as oxides, carbides, etc.). It has been found that a very fine-grain, uniformly distributed compound dispersion is most efficient in a hardening operation. Published data indicate that hardness increases linearly with the function: $1/\sqrt{\lambda}$ where λ is the average interparticle spacing. A few percent of compound dispersion would have a large effect. Bombardment by ions accompanied or followed by heat treatment could accomplish this fine-grained uniform distribution. Of course, this stable compound formation could be carried to the point where the entire surface consists of the compound rather than the base metal. More will be said on this aspect under "Oxidation Retardation" below.

D-2 Embrittlement

The hardening treatments discussed above, when carried far enough, should result in extreme embrittlement of a shallow surface layer that would then be readily removable. Thus, the ion beam might be the energy source for the embrittlement machining process postulated in Section 3.1!

Surface spalling of a material due to embrittlement and accompanying stresses as encountered in the substitutional solid-solution hardening process

described earlier appears also possible. Such a scheme could be the basis for a low-heat, material-removal process in which there are no externally applied forces.

D-3 Oxidation Retardation

Oxidation is an important limitation to the use of metals at high temperatures. In general, oxidation is rapid when the oxide product formed is porous, cracked, molten, or has a high vapor pressure. Conversely, oxidation is slow when the oxide layer is dense and adherent, constituting a good diffusion barrier. The following approaches have been used in attempts to retard oxidation:

- a. Alloying the metal to produce complex higher melting-point oxides, or lower vapor-pressure oxides.
- b. Alloying with atoms of a certain size so that a larger or smaller (as desired) specific volume oxide is obtained. (The intent is to fit the oxide to the base metal so that it is protective).
- c. Alloying to produce preferentially a very stable simple oxide (such as Cr_2O_3) which remains as a protective layer after some loss of the volatile parent metal oxide.
- d. Coating with oxide and intermetallic compounds.

Each of the approaches listed is applicable to ion beams. The alloying methods are simply extensions of the stable compound formation approach mentioned under "Hardening." Coating with oxides and intermetallic compounds can be accomplished by reducing the energy of the ion beam below critical energy for sputtering (~ 1 kv) and allowing the impinging ions to build up on the surface of the host metal. Subsequent heat treatments may or may not be necessary to stabilize the configuration.

An interesting possibility, unique to ion beams would arise if the diffusion coefficient of oxygen and/or host metal through an existing oxide layer could be lowered by the "impregnation" of foreign ions. If this is the case, then the

rapid oxidation stage reached by several metals (after the growth of the oxide to a certain critical thickness) might be avoided. Columbium and tantalum are two metals whose use is severely restricted by "catastrophic oxidation" above a critical thickness.

D-4 Further Work

We believe that ion beams have much to offer as energy sources for material modification and that their potential should be investigated by a vigorous experimental program. It may well be that now unknown relations between point defects and microscopic mechanical properties (e.g.: foreign interstitials and diffusion constant) will be uncovered which offer additional control over made-to-order material properties.

The following procedure is proposed for evaluating the surface modification schemes suggested above. Since the effect of nitrogen and oxygen on the hardness of metals is well known, an initial experiment would attempt to duplicate hardness changes by impinging high-energy ion beams of these gases upon metals. The number of ions penetrating the target, calculated from the ion current, their energy, and the change in target hardness, measured by indentation hardness, would be the principal variables. The hardened metal would also be analyzed by X-ray diffraction and electron microscopy to determine hardening mechanism, dislocation density, and penetration depth.

The appropriateness, availability and cost of the power supplies and ion-beam guns necessary for the experiments are presently under investigation. Commercially available and specially designed equipment are being evaluated. The formulation of further plans for these important experiments must await the outcome of this first design survey.

APPENDIX E

EMBRITTLMENT MACHINING

Some aspects of the machinability of metals by conventional tools are associated with the balance between flow stress and local fracture stress. The local embrittlement¹ provided by nonmetallic inclusions (such as the Fe_3C lamellae in pearlitic steel) contributes much to easy machining behavior. Conversely, uniformly soft and ductile metals (e.g., pure copper) and uniformly hard materials (e.g. a Stellite alloy) are difficult to machine.

The study reported below is based on the postulate that some type of extreme embrittlement treatment might render difficult-to-machine alloys readily machinable. The plausibility of this scheme becomes evident from consideration of the case of ceramic bodies, which are often machined in the unsintered or partially sintered condition because they fracture readily at the very small areas of bonding between grains. (A new machining process for ceramics is discussed in Section E-7.)

In order for the embrittlement-machining idea to be widely useful, it is necessary that one or a few general means of extreme embrittlement be found, and that recovery of useful mechanical properties after embrittlement be possible. The latter requirement can be avoided if one thinks in terms of localizing the embrittlement in an area to be removed, or in a surface layer. For example, embrittlement might be confined to the region just "ahead" of a cutting tool, so that no other portion of the workpiece is affected.

In our investigation, certain currently known embrittlement phenomena were surveyed with respect to generality of application, severity, reversibility of the effect, and possibility for surface or controlled-area application. The

¹Brittleness is defined simply as fracture without plastic deformation; a material may be either weak and brittle, like common glass, or strong and brittle, like a very high strength steel. Embrittlement will be used in its engineering sense to mean a decrease in fracture strength under at least one type of load, e. g. under impact loading.

results are summarized in Table E-1. Details of the evaluation are included in the discussion of the embrittlement types below. A recently discovered scheme for embrittlement machining of certain ceramics is then presented, and the extension of its principle to other cases is discussed. Finally, recommendations are presented for experimental investigation of embrittlement phenomena found promising in the present study.

TABLE E-1
EVALUATION OF EMBRITTLEMENT SCHEMES

Embrittlement Type	Generality of Application	Severity	Reversibility	Controllability
Direct Second Phase	Poor	Good	Poor	Fair
Gaseous	Good	Good	Good	Good
Low Temperature	Fair	Poor	Good	Good
Surface	Good	Fair	Good	Good

E-1 Discrete Second Phase Embrittlement

Graphitic cast irons are known as very easily machined materials. The good machinability is largely attributed to the presence of discrete graphite flakes or nodules, which provide local stress concentration and brittleness. The gray fracture surface of such alloys attests to the fact that the flakes or nodules of graphite provide paths of easy fracture. Energy absorption in the standard Charpy V-notch impact test for cast irons is about 3 ft-lbs, which may be compared (33) with the value of 100 ft-lbs for 1020 steel above 50°C.

The matrix (iron) phase in cast iron contains carbon in solid solution (ferrite) or, alternatively, consists of ferrite + Fe_3C (pearlite) and in either case will be rather tough. In the absence of the brittle graphite phase, such a material would be much more difficult to machine.

Although cast irons are a prime example of embrittlement machining in practice, discrete second-phase embrittlement does not seem promising as a general technique. Its generality of application is poor; a precipitating weak and brittle phase would have to be found for each of a large number of alloy types.

With appropriate weak and brittle phases, the severity of the embrittlement is good. The reversibility is poor because the precipitated phase will generally be thermodynamically stable and will appear repeatedly on cooling slowly from any elevated service or heat-treatment temperature. Actual removal of the constituents of the phase by diffusion might be possible, but would be very time consuming. Controllability is fair as constituents of a weak and brittle phase might be diffused into the surface of a piece. Such diffusion would be slow, however,

E-2 Beryllium Embrittlement

Beryllium affords an opportunity to examine the machining behavior of a single-phase metal which is very brittle in any commercial form. It is so brittle that strength-test specimens must be carefully machined and chemically etched to remove surface damage if strength values representative of the bulk material are to be obtained. Loads are carefully applied to obtain purely uniaxial stress because under bi- or triaxial stresses, virtually all plasticity is lost. A typical value of energy absorption during impact failure for an unnotched specimen is about 1-in.-lb at room temperature, 1/40 that of cast iron, and equal to that of alumina ceramic (33).

According to Olofson (34), beryllium machines like cast iron, except that it is somewhat more abrasive to tools. Coarse-grained cast and fine-grained hot-pressed beryllium seem to machine alike. Chip formation in machining beryllium is primarily a brittle fracture process. The chips are found to be discontinuous segments which tend to "reweld" to one another after separation from the work surface. Carbide tool life is comparable to that obtained in machining carbon steel.

Thus, beryllium, an extremely brittle single-phase metal is easily machinable; therefore, its mechanical properties are of interest. The brittleness of beryllium was attributed to a film of oxide at the grain boundaries until relatively pure metal was found to fracture transgranularly at low stress. Brittleness in beryllium is now known to be largely due to the fact that only one crystallographic system of easiest slip exists in the hexagonal crystal, and only about one-percent strain occurs before fracture (35). The easily operated

slip system is in the basal plane. The only other slip system operating at room temperature is in the $(10\bar{1}0)$ prism plane, having the same slip direction as the basal slip system, so that slip parallel to the c-axis does not occur in either case. The remaining fundamental question is to what extent removal of all impurities will increase the elongation and decrease the brittleness of beryllium.

The applicability of the brittleness mechanism of beryllium to other metals is similar to that of second-phase embrittlement in cast iron: The practicability of machining an extremely brittle metal is substantiated, but the mechanism is not generally applicable. Since the embrittlement mechanism involves either inherent or impurity controlled limitation of slip on all but one or two crystallographic planes, it appears that only a very detailed study of each of many alloy types will lead to duplication of the behavior of beryllium in machining.

E-3 Gaseous Internal Embrittlement

Many forms of gaseous embrittlement are known. Since they often involve grain-boundary embrittlement and are sometimes subject to control by heat treatment, they are particularly interesting in our search. Various forms of hydrogen embrittlement will be discussed first (E-3.1) then, other types of internal gaseous embrittlement will be listed (E-3.2).

E-3.1 Hydrogen Embrittlement

According to Rogers (36), the metals subject to H_2 embrittlement may be categorized as exothermic occluders and endothermic occluders. The former are characterized by large H_2 solubility, definite hydride compound formation, and a negative heat of solution which results in a solubility decrease with increasing temperature. Exothermic occluders include vanadium, titanium, zirconium, tantalum, thorium, and cerium. Endothermic occluders such as iron, cobalt, copper and nickel have a lower H_2 solubility, which increases as temperature increases. H_2 may embrittle metals by H_2 attack, by hydride embrittlement or by the hydrogen embrittlement, as discussed in the following paragraphs.

E-3.1.1 Hydrogen Attack

H_2 reacts with a second phase or high local concentration of a minor element, usually at the grain boundaries. In silver, copper, and low-carbon iron, H_2 reacts with oxides to form water-vapor. The pressure of the water vapor and the accompanying oxygen depletion result in severe intergranular damage. In steels, H_2 reacts with carbides to form methane, producing similar damage. The magnitude of embrittlement readily attained in copper is such that a sample of copper originally containing 0.008 percent O_2 had only 5000 psi tensile strength with zero elongation after embrittlement.

E-3.1.2 Hydride Embrittlement

Many exothermic occluders form definite hydride compounds internally, making the metal increasingly brittle with increasing H_2 content, decreasing temperature, and increasing strain rate. The hydride in titanium alloys takes the form of platelets in the alpha phase or of a grain boundary precipitate. (Note that this type of H_2 embrittlement is essentially a second-phase embrittlement. The categories of embrittlement used herein are quite arbitrary, and overlap.) According to Williams (37), commercially pure titanium containing 2.5 atomic percent H_2 and cooled slowly to allow maximum hydride precipitation has a notched impact strength of about 3 in.-lbs. (Compare with the value of 55 in.-lbs for quenched titanium having the same H_2 content.) The absorption of H_2 by exothermic occluders is readily reversible. For titanium, heating to about 1300°F in a good vacuum will lower the H_2 content to < 100 ppm.

E-3.1.3 True Hydrogen Embrittlement

This form, known as "low-strain-rate embrittlement" in the titanium industry, occurs in iron, steel, titanium and its alloys, and vanadium. H_2 must be present in the metal during the deformation which reveals the embrittlement. The mechanism of the embrittlement is controversial. Eustice and Carlson (38) propose that in vanadium, the embrittlement is due to dislocation impediment in a critical temperature causing the

yield stress to become nearly equal to the cleavage stress. However, a different mechanism must operate in steels, since the yield stress is not increased. Whatever the mechanism, the uniform tensile elongation of vanadium at -40°C is reduced from 20 to about 0.5 percent by 800 ppm of H_2 . According to Troiano (39), steels, columbium, molybdenum, and tantalum are also susceptible to "low-strain-rate embrittlement" and any of the interstitial elements, such as hydrogen, oxygen, carbon, nitrogen and boron can cause it. Troiano proposes that hydrogen diffusing to the region ahead of a crack tip reduces the cleavage stress of the crystal lattice. The diffusion mechanism is plausible, since the embrittlement is not found at high strain rates, which would require too rapid diffusion. As with the previous embrittlement type, the absorption process is reversible.

E-3.2 Internal Embrittlement by Gases Other Than H_2

Various gases react in the grain boundaries with metal or segregated phases to produce damage analogous to that described above as hydrogen attack, i. e. damage due to high pressures. One example is that of oxygen in some of the refractory metals. Browning (40), states that a "principal difficulty in fabricating tungsten and molybdenum by conventional means is the severe embrittlement which occurs upon heating above the recrystallization temperature." It is believed that oxygen diffuses into the grain boundaries and forms the oxide of the parent metal. Since the oxides of the refractory metals tend to have high vapor pressures far below the melting point of the metal, void formation and severe embrittlement occur. Oxide films at the grain boundaries also cause severe embrittlement even at low temperature where the vapor pressure is not a factor. Particularly in molybdenum and tungsten, oxide film embrittlement is an important problem. Goodwin (41) notes that the great importance of fine grain size in several metals lies in the fact that the finer the grains, the greater the grain boundary area over which impurities (including oxides) are spread, and the less is the embrittlement.

In summary, the applicability of gaseous internal embrittlement to various materials is good; since several types of gaseous embrittlement are

known and many metals are affected, such embrittlement processes might be widely applicable. At least for some types of gaseous embrittlement, the severity of the effect is good. Reversibility is good; many metals will take up H_2 at low temperature (e.g. in an electroplating bath) and will release H_2 at higher temperatures; others behave oppositely. Of course, the type of gaseous embrittlement involving grain boundary damage would not be so readily reversible. Controllability is good, especially if the embrittlement can be made to occur rapidly in the surface layer ahead of a cutting tool.

E-4 Low Temperature Embrittlement

Body-centered cubic metals such as iron, chromium, molybdenum and tungsten exhibit an abrupt change from ductile to brittle behavior on cooling. The hexagonal close-packed (zinc, cadmium), body-centered tetragonal (tin) and body-centered rhombohedral (bismuth) lattices behave similarly (42). The ductile-to-brittle transition is manifest by a change in failure mode from "tearing" (shear) to cleavage or grain boundary fracture, and a very large reduction in ductility as measured by several parameters. The transition occurs in the temperature range where yield strength increases rapidly with decreasing temperature. According to Wells and Triplett (43) when the yield stress becomes sufficiently high, the energy absorption due to plastic deformation during crack propagation becomes almost nil. Thus, the measured impact energy absorption below the transition temperature appears to be simply a crack formation energy, while the value obtained above the transition temperature is a sum of crack formation and propagation energies. A factor affecting yield or fracture stress will shift the transition temperature. Increasing strain rate, which increases the yield stress, raises the transition temperature markedly.

Certain embrittlement phenomena are revealed only by their effect upon transition temperature. Temper brittleness in steels, believed to be due to impurity segregation at prior austenite grain boundaries, is a case in point. The increase in transition temperature (about 50° to 200°F) becomes significant if the new transition temperature is above the minimum temperature of actual use of the steel.

Examples of decrease in impact energy absorption associated with the transition from ductile to brittle behavior for notched bars are: 1020 steel, 120 ft-lbs to 5 ft-lbs; molybdenum, 130 ft-lbs to 8 ft-lbs; chromium 118 ft-lbs to 1.5 ft-lbs (41). The temperatures of transition for the cited samples were about 18°F for the steel, 550°F for the molybdenum, and 450°F for the chromium.

In the case of low-temperature embrittlement, it is possible to get some indication of the potential for "embrittlement machining" from existing literature on low-temperature machining of steels. Pentland (44) noted that in turning AISI 4340 steel, tool forces dropped from about 500 lbs to 300 lbs when the workpiece was cooled below 0°F, and the tool-chip interface temperature dropped from about 1300°F to 1000°F on cooling from +100°F to -100°F. Low-temperature brittleness in this steel could very well occur below 0°F, and thus might account for the improved machinability. On the other hand, Pentland found that the lowest of four cutting speeds produced the greatest reduction in tool forces and interface temperature. This finding is apparently contrary to what would be expected.

In an Air Force supported study, low-temperature machining tests were performed with several high-strength alloys (45). Cutting speed and/or tool life was increased 50 to 300 percent. Again, it should be pointed out that embrittlement is only one of the possible explanations, and that systematic investigations of the embrittlement mechanism and of resulting material-removal behavior have not been reported.

In summary, the generality of the low temperature embrittlement effect is fair; many of the alloys of interest are susceptible. Its severity is poor, but in conjunction with other embrittlement means, and considering the experimental indications, perhaps adequate. If the use temperature is above the transition temperature, reversibility is good. Because a surface layer or area is readily cooled, the controllability of low-temperature embrittlement schemes would be good.

E-5 Surface Embrittlement by Liquids and Gases

In addition to the internal embrittling effects of gases, there is a type of surface embrittlement caused by the mere presence of certain gases and liquids on metal surfaces, in conjunction with stress. The effect is not to be confused with normal intercrystalline penetration by liquids or gases in the absence of stress, or with surface reaction to form brittle compounds. Both of these are more gross effects than those of concern here. Rather, the effects appear to be due to surface energy reduction by adsorbed atoms. Rostoker et al. (46) have studied the subject of liquid-metal embrittlement in detail and believe that various liquids and gases have the same effect as liquid metals; therefore, we will discuss liquid-metal effects almost exclusively. Interestingly, Rostoker et al. also speculate as follows: "conceivably, the use of liquid metals could improve the machinability of hard alloys; in fact, the harder the alloy, the more effective the process should be."

Perhaps the best known example of this type of embrittlement is the disintegration of internally stressed alpha brass in mercury. Rostoker et al. (46) also cite the following examples: steel embrittled at 1000°C by tin, zinc, antimony and brass alloys; aluminum alloys embrittled by mercury, gallium, sodium, tin, and zinc; titanium alloys embrittled by mercury and cadmium. The magnitude of embrittlement is large; e.g. 4130 steel at a hardness of $R_c 50$ normally has an ultimate tensile strength of about 235,000 psi, but when wetted with lithium the fracture strength is about 40,000 psi. The harder the material, the greater the reduction in strength and the lower the absolute value of the fracture strength.

Crack velocity measurements have shown that liquid metal cracking is sometimes a rapid process; e.g. crack velocity in 2024-T4 aluminum wetted with mercury was about 300 in./sec. However, the data on this aspect of the phenomenon show much variance.

Rostoker et al. (46) proposed that the mechanism of embrittlement by liquid metals consists simply of crack-surface-energy lowering by adsorption. That is, in the applicable fracture mechanics equation for fracture "nuclei" formation, the effective surface energy (which opposes fracture) is greatly reduced by adsorbed atoms. The nongeneral occurrence of the embrittlement

(only a few liquid metals cause embrittlement in a given alloy type) is explainable on the basis of surface energy relations. However, in the absence of adequate surface energy data, it has been found that the factor which correlates best with embrittlement is mutual insolubility. Embrittlement is not found in couples having mutual solubility.

As suggested by Rostoker et al. many forms of stress corrosion may operate by the mechanism outlined above. Examples include the cracking of brasses in ammonia gas, of steels in sodium hydroxide and hydrogen cyanide, and of magnesium in sodium chloride solutions. However, some stress corrosion failures occur very slowly, suggesting differences in mechanism. At any rate, various metals are subject to brittle failure due to interaction with the environment.

The evaluation criteria apply as follows: The generality of liquid and gaseous surface embrittlement is good; at least one embrittling agent should be available for most metals. Its severity is fair; if the process requires only very shallow penetration, severity is adequate. Reversibility is good in the sense that the damaged surface would be easily removed mechanically or chemically. The embrittlement is a surface or near-surface phenomenon; therefore, its controllability should be good.

E-6 Radiation Embrittlement

Embrittlement of materials by nuclear radiation is known to occur and is known to be reversible. Bombardment by particles such as protons, deuterons, and alpha particles - or neutrons - appears necessary to achieve useful rates.¹ The artificial radioactivity introduced in the workpiece could be a deterrent to the practical use of radiation embrittlement. Also, it appears that the embrittlement is not generally great even with large dosages of radiation. According to Billington and Crawford (47), the effect of

¹A more general discussion of material modification by neutron irradiation appeared on pp. 29-32 of the first Interim Technical Report.

10^{20} nvt¹ neutron irradiation on a carbon-silicon steel is to shift the low transition temperature for embrittlement from about 20°F to 130°F, with little reduction in impact energy absorption. Billington and Crawford also mention the possibility of severe damage due to helium fission gas production from boron segregated in the grain boundaries of a steel. Such possibilities warrant further study.

E-7 Embrittlement Machining of Ceramics

The machining of unsintered or partially sintered ceramics was cited as a basis for the idea of embrittlement machining in metals. However, the shrinkage which accompanies the further sintering of machined parts severely limits the applicability of this process. Elimination or near-elimination of post-machining shrinkage would constitute an order-of-magnitude improvement in ceramic forming.

Of course, practical ceramics always fracture in an entirely brittle manner at ordinary temperatures, and unsintered or partially sintered material fractures at low stress because the real area of contact and bonding between grains is relatively small. In turn, the contact area is small because the irregular particles making up the compact fit together very imperfectly before the shape adjustment and void-elimination processes of sintering.

To eliminate shrinkage, methods must be found for lowering the fracture strength after sintering without reintroducing voids. Such a method has been discovered by Buessem and Marshall (48). In the course of a study of dielectric ceramics, they found that hydrofluoric acid vapor changed alumina ceramics to a weak, easily powdered material. Resintering the weakened material resulted in strength recovery without appreciable dimensional change.

The mechanism of weakening appears to be the dissolution of impure alumina at the grain boundaries. Apparently the actual volume of material lost is so slight that no appreciable change in size occurs upon firing to regain strength. It may be speculated that a suitable "solvent" exists for

¹The quantity nvt, the product of number of neutrons, their velocity and total time, is a measure of total neutron flux.

most commercial ceramics, since segregation of impurities in the grain boundaries is the rule rather than the exception. Further investigation with a view toward commercial exploitation is planned according to Professor Buessem (49).

Another possible means of embrittling ceramics involves the combined effects of stress and liquid or gaseous environment. The mechanism of embrittlement is thought to be the same (i. e., surface-energy lowering by adsorption) as that which occurs in liquid metal embrittlement of metals. Data are meager, but strength reductions up to 50 percent over a long-time application of load have been found. The weakening, usually termed static or atmospheric fatigue in ceramics, is apparently caused by water vapor in normal atmospheres (50, 51). Further data on the effects of temperature and composition are needed before the potential of atmospheric fatigue in ceramic machining can be evaluated.

E-8 Recommendations

Several of the embrittlement phenomena examined are quite general, severe, readily reversible, and adaptable to a controlled surface or "ahead-of-the-cutting-tool" application. In particular, some types of hydrogen embrittlement, liquid metal, and other "environmental" treatments appear promising.

In view of the incomplete understanding of embrittlement phenomena and of machining processes, our studies must be supported heavily by experiments. Also, a search will have to be made for appropriate measures of embrittlement that will permit evaluation short of actual machining tests.

The schemes for surface hardening and embrittlement by bombardment discussed in Section 3.2 and Appendix D are particularly attractive candidates for an experimental program. However, it is recommended that other embrittlement methods, e. g. by liquid metals, also be investigated.

The effect of nuclear radiation on the brittleness and material removal behavior of body-centered cubic and face-centered cubic metals at various temperatures and over a large range of strain rates also is worth investigation.

APPENDIX F

DIRECT DEPOSITION PROCESSES

Directly deposited self-supporting structures and coatings are formed by continuously additive processes. The added units may be atoms, molecules, droplets, or solid particles. Thus, the physical state of the additive may be gaseous, liquid or solid. A large number of basic processes and variations have been used over the years, but exploitation and development have been slow.

The types of structure produced by available direct deposition methods are discussed with respect to mechanical property and configuration control factors, and ways of changing properties and controlling shape are suggested. The discussion is only exploratory and is to serve as a basis for and stimulus to further project effort on direct deposition processes.

Process rates, although a very important factor in evaluating potential, are not discussed at this time because they depend to a great extent upon the nature of the desired product.

F-1 Deposition Methods

Almost all direct deposition methods fall into five broad categories, which are discussed in turn.

F-1.1 Growth from Melts

Any process by which single or polycrystalline materials are grown with the growth interface in contact with molten material of the same composition may be classified as growth from the melt. In general, the techniques consist of:

- a. "Pulling" a crystal slowly out of a melt (Czochralski method).
- b. Passing heater rings horizontally over an ingot of material in a crucible, so that molten "zones" pass slowly along.

- c. Passing heater rings up over a vertically supported ingot to produce a "floating zone" of molten material which is held in place by surface tension (no crucible).
- d. Dropping molten droplets of material onto the top of growing crystal (Verneuil or flame-fusion process).

The casting process, though topologically a growth-from-melt process, is not of interest in the present discussion.

F-1.2 Growth from Solutions

Strictly speaking, all melts are solutions (since some impurity level, however small, is always present), and we could consider the growth of the solvent phase or the solute phase from a solution. Thus in what is commonly called "melt growth," solvent-phase growth is the more proper designation. However, we shall maintain separate categories, treating solvent-phase growth from dilute solutions as melt growth.

Any means of causing a solid to precipitate slowly onto a substrate or seed crystal from an appropriate solvent can be used. Such methods include cooling a saturated solution, electrolytic plating (in this case, ions of a desired metal are reduced at an electrode to the metallic state), and catalytic reduction. In the last-named process, reduction of metallic ions is brought about by an added reducing agent through catalytic action of the substrate surface. The so-called "electrodeless" plating of nickel in this manner is a much-used process. Nonmetallic surfaces can be made catalytic to chemical plating by immersing them in certain ionic solutions; e.g., palladium chloride solution for nickel plating.

The "hydrothermal" process for the growth of quartz and other nonmetallic crystals is comprised of the following elements:

- a. Action of water, heat, pressure, and a chemical additive in dissolving the substance to be grown (in an autoclave)
- b. An appropriate seed crystal

- c. Control of temperature gradient in the solution so that "feed" material is dissolved in one portion and precipitated on the cooler growing crystal

F-1.3 Growth from Vapors

Thermal evaporation in a vacuum provides a stream of atoms or molecules of the evaporant element or compound. Condensation will occur on any cool surface in the vapor path. Atmospheres (in contrast to a vacuum) tend to react with and scatter the evaporant. Vapor deposition is the term generally applied to processes in which a volatile compound is carried in a gas stream to a heated substrate, where pyrolysis and deposition of a constituent of the compound will occur. Many metals, carbides, nitrides, borides, oxides, and other compounds can be deposited in this way. A variation consists of depositing one constituent of a compound of which the substrate is the other constituent; thus, Si deposited on carbon produces a SiC coating. Heating is necessary in the latter case not only for pyrolysis but for diffusion of substrate material atoms to the reaction zone.

F-1.4 Deposition from Suspensions

Sufficiently fine particles of solid material can be suspended in liquids and moved to the surface of a substrate in a controllable manner. In spraying, the liquid is broken into droplets and propelled by gas streams or mechanical forces to the substrate, where liquid is lost into the substrate or the surrounding atmosphere. An electrical charge may be imposed upon droplets and substrate to increase the efficiency of transfer of droplets to the substrate.

In dipping processes, the wetting of the substrate by the liquid vehicle is relied upon to form a coating, or electrophoresis may be employed. Recently, high-velocity gas streams have been used to "fluidize" beds of particles where temperatures were too high for convenient liquid suspension.

F-1.5 Hot Spraying

Various types of flame guns have been used in the past to heat and/or melt particles, rods, or wires of metals and ceramic materials and simultaneously to propel the particles or molten droplets to a substrate surface. The advent of plasma gun spraying has much improved the flexibility of the process by raising available temperatures and by providing atmosphere (reduction-oxidation) control.

F-2 Factors Controlling Strength

Outlined below are the elementary factors which control the strength of metals and ceramics built up by such processes as are mentioned above. The outline provides a basis for the ensuing discussion of properties and configuration control for each growth method.

F-2.1 Metals

F-2.1.1 Crystal Structure

Ductility in metals is due largely to the presence of line defects in the crystal lattice (dislocations). These defects can move under the action of a shear stress of magnitude determined by atom sizes, packing, and bonding, provided that impurities and grain boundaries are not present. If impurities, grain boundaries (or even a large number of dislocations) are present, dislocation motion is impeded and the yield stress thereby increased.

In the absence of all dislocations, grain boundaries and surface flaws, shear flow will not occur at any stress prior to fracture. Fracture will occur at extremely high stresses determined by crystal structure and bonding.

Obviously, conventionally produced metals exhibit behaviors dominated by the impurities, grain boundaries and dislocations present. However, it will be seen in the discussions of crystal growth that crystals free of dislocations and flaws can be produced, do have high strengths, and may therefore become of great importance.

F-2.1.2 Impurities

Even uniformly distributed impurity atoms disturb the regular crystal lattice and thereby impede dislocation movement (solid solution strengthening). Clustered or precipitated impurities are also effective hardeners. On the other hand, an appreciable concentration of impurities at the grain boundaries of a polycrystalline material is likely to provide a path of easy fracture.

F-2.1.3 Porosity

Porosity has a large strength-reducing effect, especially in rather brittle metals. The effect is much larger than can be accounted for from the reduction of real cross-sectional area. For very brittle deposits the fracture strength can probably be approximated by the empirical equation

$$S = k G^{-a} e^{-hP}$$

where S = fracture strength, psi
 P = volume fraction porosity
 G = grain size in microns
 k , a , and h are empirical constants
 e = natural log base.

This type of equation was found by Knudsen (52) to fit many data on brittle metals and ceramics. For example, a series of hot pressed chromium carbide specimens had flexural strengths between 22,000 and 55,000 psi. Corresponding equation parameters were:

P = 10 to 0.6 percent
 G = 6.5 to 15.0 microns
 k = 228,000
 a = 0.56
 h = 6.5 to -4.6

F-2.1.4 Grain Boundaries

Grain boundaries impede dislocation movement and also tend to stop crack propagation. Thus, for most materials, the greater the total area of grain boundary (i.e., the smaller the grain size) the greater are both the yield and fracture strengths. Unfortunately, creep becomes an important failure mechanism at high temperatures, and a large grain boundary area favors creep. (Creep can occur by dislocation climb, i.e. dislocation movement other than in slip planes. Grain boundaries apparently provide paths of easy climb at elevated temperatures.) For very brittle structures, grain size affects strength in a manner represented by the preceding equation with "a" approximately 0.5,

F-2.1.5 Cold Work

Cold work or strain hardening is an important contributor to the strength of most cold-formed metal articles. The mechanism of strain hardening involves the multiplication and interaction of dislocations. (A more detailed discussion appears in Appendix G.)

F-2.2 Ceramics

F-2.2.1 Crystal Structure and Binding

Engineering ceramics do not exhibit plastic flow at temperatures much below their melting point because of the complex nature of their structure and atomic binding. Factors militating against slip are the structural complexity due to the presence of two or more ions unlike in size and charge, and the presence of directional (covalent) bonds. These factors are minimized in cubic, highly ionic materials such as the alkali and noble-metal halides and MgO, which tend to show some ductility at room temperature, at least in single-crystal form.

It might seem that the useful fracture strength of engineering ceramics would be controlled by the atomic binding forces. However, binding forces are actually important only when nearly all surface and

other flaws have been eliminated. Flaws thus constitute "weak links" in real bodies. The nominal stress required to extend a flaw depends upon the stress concentration factor due to flaw size and shape, and is "opposed" by specific surface energy of the new surfaces formed by flaw (crack) propagation. Gaseous and liquid environments can lower the stress necessary for crack propagation by adsorbing on the fracture surfaces, thereby lowering the effective surface energy.

F-2. 2. 2 Grain Boundaries and Porosity

These factors have an effect which can be described by the Knudsen (52) equation given previously. Grains in the best commercial bodies are less than ten microns in average size. It is thought that grain boundaries may limit crack propagation. Another strengthening effect of small grains is due to the minimizing of internal stresses due to thermal expansion anisotropy in bodies composed of noncubic crystals.

F-2. 2. 3 Impurities

Small amounts of impurity in solid solution have little effect. However, impurities in the form of glass at the grain boundaries tend to weaken a dense body that would otherwise have rather perfect crystal-to-crystal bonding. (e.g., a 99.5-percent alumina body having a trace of glass in the boundaries may have a flexural strength of 60,000 psi, while a 97.6-percent alumina body may have a strength of about 45,000 psi.)

F-2. 2. 4 Surface Stress

Because the common mode of failure of ceramics is surface tensile fracture rather than shear or compressive deformation, it is possible to gain effective strength by treating parts so as to place all surfaces under compression. Any applied tensile stress must then exceed the residual surface compression before the surface actually experiences tension. The

surface compression can be developed by rapid cooling as follows: the cooled surface becomes rigid first and shrinks according to its thermal dilation coefficient while the interior is still near melting and can therefore deform viscously or plastically. The interior thus accommodates the shrinkage of the surface to a degree without stress development. Upon continued cooling, the surface reaches room temperature first while the interior still must cool and shrink rigidly. Compression in the surface and tension in the interior develop.

Another (little-exploited) method of achieving surface compression consists of diffusing into the surface large atoms which expand the crystal lattice slightly. Corning Glass Company has announced such a process for application to "glass ceramic" materials.

F-3 Properties and Configuration Control

F-3.1 Growth from Melts

F-3.1.1 Properties of Single Crystals

The atoms of a liquid are very mobile, and those on the growth surface of a solid in contact with melt are thought to be only slightly less so. Because of this ready surface diffusion, most of the atoms "solidifying" are able to take up their proper equilibrium positions in the lattice. In fact, the calculated dislocation concentration for single crystals is only one dislocation per $10^{16,000} \text{ cm}^2$ crystal area (53). However, it is known that lattice vacancies form in large numbers even during slow-melt growth, and according to Howe and Elbaum (53), groups of these vacancies cause dislocation formation unless they are allowed time during growth to diffuse to surfaces. Shear stresses between rotating crystal and melt (in the Czochralski method of growth by pulling vertically) also appear to cause surface dislocation formation, and any crucible growth method introduces many surface dislocations due to constraint by the crucible.

Internal dislocations should also tend to arise from thermal contraction strains, strains due to impurity concentrations, and misorientations when dendritic growth occurs.

Howe and Elbaum conclude that freedom from dislocations can be expected only in slowly grown whisker-size crystals, and this is the observed fact. Whiskers of several compounds and metals have been grown (many from vapor rather than melt) without detectable dislocations. As predicted, these whiskers do not deform plastically, and if their surfaces are nearly free of flaws, they exhibit tensile fracture strengths of up to about 6 percent of the elastic modulus (54).¹ (~ 1.9 million psi for iron whiskers.)

It appears that monocrystals larger than whiskers cannot be grown slowly enough to avoid vacancy group formation, and in turn, dislocation formation. Thus, large metal single-crystals always contain at least a few dislocations and tend to be among the weakest materials known. Yield stresses below 30 psi are measured for pure zinc monocrystals, for example. The reason for the extreme softness is, of course, that these crystals lack all hardening imperfections, even the mutual interference developed when many dislocations are present.

In another special category of single crystals, dislocations cannot move. These are the largely covalently bonded materials such as certain oxides, silicon, metal carbides, and intermetallic compounds. The directionality and strength of bonding leads to theoretical plastic flow stresses greater than the ultimate fracture strength (i. e., 5 to 10 percent of the elastic modulus). Gilman (55) feels that "the ultrahigh-strength materials of the future" have strengths in this category. He has measured fracture strengths of about 500,000 psi in 1/16 sq in. monocrystal silicon "hairpins" having carefully prepared surfaces. However, he points out that these crystals are perfectly brittle (they have extremely high strength because they are not ductile). Unfortunately, a brittle material is vulnerable to surface damage by impact loads, surface scratches, and the like, so that it must be protected with a ductile coating if high strength is to be obtained.

¹The elastic modulus represents the force required to pull atoms apart. When atomic bonds are stretched 5 to 10 percent, attractive forces are small. Thus, as a first approximation, the ultimate possible strength of a solid is 5 to 10 percent of the elastic modulus.

In practice, in many ionic crystals (many ceramics) dislocation movement is observed or predicted at high stress, and, also, surface flaws have been present in larger-than-whisker-size crystals that have been tested. Thus, measured fracture strengths are comparable to those of dense, fine-grained polycrystalline bodies of the same compound.

To summarize the general mechanical behavior of nearly perfect crystals, most metals, when free of dislocations and surface flaws, show extremely high strengths, but can be produced only in small "whiskers," according to reference (53). Most metals, when pure but containing a few dislocations, show extremely low strengths.¹ Normally brittle materials, especially those which have covalent bonding and nearly flaw-free surfaces, can show extremely high strengths even when they have dislocations that cannot move.

F-3.1.2 Properties of Polycrystals

As described above, special types of single-crystal offer useful high (or "superhigh") strength possibilities, provided that their surfaces can be protected. However, the straightforward approach to useful strengths by direct deposition is to duplicate existing polycrystalline alloys. This approach, under study for ASD by American Machine and Foundry Company (56) must involve control of grain structure and impurity distribution. It is possible to control the level of soluble impurities by controlling crystal-pulling rates or zone passage rates in molten zone techniques, by virtue of the fact that a given impurity tends to have a different equilibrium solubility in solid and liquid solvent phases of the same nominal composition. Insoluble impurities for dispersion hardening might be difficult to add in pulling or zone-growth methods, but could be added readily in the Verneuil process, in

¹An exception to the "rule of extremely low-yield strength in pure metal single crystals is the group of materials, especially tungsten and beryllium, which tend to be brittle in ordinary forms. Pure single crystal of these materials are more workable than less pure forms, but retain useful strength.

which molten droplets are allowed to fall on the growing interface. Grain boundaries might be produced in a grown material by vibratory (ultrasonic, perhaps) disturbance of the growing interface.

F-3.1.3 Configuration Control

The tendency in any single-crystal growth process is for the fastest growing crystal faces to "grow out of existence," leaving the slow-growing face to continue, as in Figure F-1. Use was made of this phenomenon to grow long ribbons of semiconductor material suitable for transistor fabrication, and other shapes would be possible (57). Growing "branches" in certain crystallographic directions should be possible, but probably not without boundary and dislocation introduction.

In vertical growth methods, cross-section size depends on temperature, and pull or droplet rates so that cones and tapered cylinders are producible at present. When a crucible is present, the shape of the ingot generally is that of the crucible.

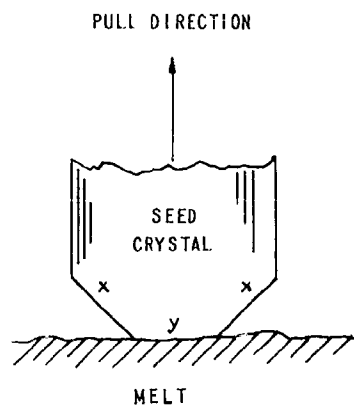
Another broad control possibility exists in the realm of electrical and magnetic fields, which might be used to shape ionic and magnetically susceptible melts, respectively. In the event that defect-free crystals become important, such "no-hands" shape control would be necessary.

Another simple expedient by which "branching" might be controlled is mechanical damage. Minute disturbance of a crystal surface by a probe tends to cause a new crystal branch to grow. Mutual damage in two crystals will cause them to bond together. The possibility of introducing motion in one or more directions and the use of shields or barriers to starve certain sites was suggested earlier (58).

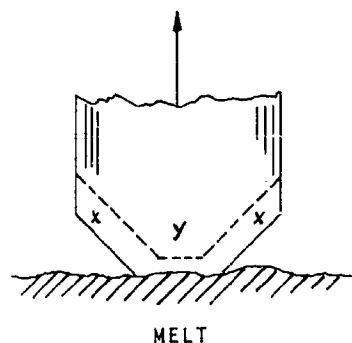
F-3.2 Growth from Solutions

F-3.2.1 Properties

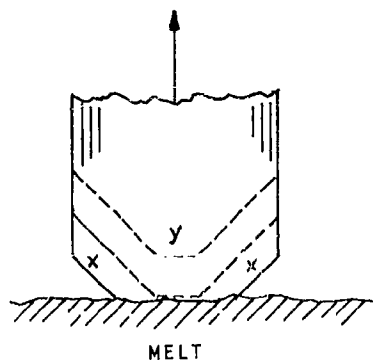
Electro- and chemically plated deposits tend to be very imperfect on the atomic level, in that they contain impurities and a high



(a) FACES MARKED "x" ARE FASTER GROWING THAN "y"



(b) DOTTED LINES MARK FORMER SHAPE



(c) AFTER A CERTAIN TIME INTERVAL, THE "x" FACES HAVE VIRTUALLY DISAPPEARED, AND GROWTH WILL CONTINUE PERPENDICULAR TO THE "y" FACE

Figure F-1 NATURAL CRYSTAL GROWTH

concentration of the various lattice defects. These imperfections and the residual stress which often develops causes platings to be hard, a feature which is often beneficial where wear resistance is desired. Co-deposition of elements to form solid solutions is readily possible in many cases. For example, chemically plated nickel contains 5 to 10 percent phosphorus when plated from a solution containing a pyrophosphate reducing agent.

Nonmetallic crystals grown slowly on seeds (e.g., quartz, rochelle salts) tend to be fairly perfect, but less so than melt-grown crystals. The Armour Research Foundation has developed a series of solutions from which polycrystalline (or nearly amorphous, as deposited) coatings of various ceramics can be deposited.¹ Attractive properties, such as good thermal shock resistance and adherence are claimed, but as in any coating system, depend heavily upon the nature of the substrate.

F-3.2.2 Configuration Control

The shape of electroplated parts is subject to some control by electrode placement. Rectangular waveguides of closely controlled internal dimensions are produced by electroplating on mandrels (forms) which can subsequently be melted or dissolved away. The fabrication of accurate external shape should be possible if deposition is made on the inside of hollow forms.

Crystal growth from solution is particularly sensitive to catalytic and "poisoning" effects. The latter refers to adsorption of an impurity on a growing interface with consequent slowing of growth. It is possible to visualize shape control by controlled catalysis and poisoning since both tend to occur preferentially on certain crystal planes.

¹"Solution Ceramics," Armour Research Foundation, Brochure, No Number, No Date.

F-3.3 Growth from Vapors

F-3.3.1 Properties

Whiskers having extremely high strengths can be grown by vapor deposition (their properties discussed in Section 5.2.3.1). Films produced on cold substrates by thermal evaporation tend to have less than the theoretical maximum density due to the instant immobilization of atoms as they strike the substrate.

Pyrolytic deposition offers attractive properties even though the anisotropy of pyrolytic graphite will be found in few other materials. Graphites having strength, thermal conductivities, and electrical conductivities which are anisotropic by two or three orders of magnitude have been produced by vapor deposition. Pyrolytic hexagonal boron nitride was similarly produced. However, it should be remembered that materials having a high degree of crystalline anisotropy are rare. In the long run, the importance of chemical vapor deposition processes may be that dense, strong sections of almost any material can be produced at relatively low temperatures.

F-3.3.2 Configuration Control

Control of thickness at a given point should be possible by controlling gas flow to the area and/or the temperature of the area. Laminates of several materials should be readily producible by vapor deposition. Whiskers of Al_2O_3 having a "core" of aluminum metal have been grown by DeVries of the General Electric Company.

F-3.4 Deposition from Suspensions

F-3.4.1

The products, such as sintered metal coatings on ceramics, glass coatings on metals and ceramics, and composite coatings on metals for oxidation protection, tend to be porous unless binders are present,

or sintering/melting treatments are applied. Even with sintering/melting treatments, residual porosity is present. In one case (the sintered metal coatings on ceramics used in ceramic-metal bonding), the porous layer provides a matrix into which a glassy bonding material on the "ceramic side" and a metal braze on the "metal side" can penetrate.

Deposition of mixtures of particles which can be converted into conventional or dispersion strengthened alloys appears to be a more straightforward process by particle deposition methods than by the other deposition processes which have been discussed. Control of deposition by the action of electric fields on charged particles is, of course, a reality in electrophoresis, but probably can be developed into a much more flexible tool.

Progress in the fabrication of lathe tool inserts by electro-phoretic deposition of boron-modified carbide coatings has been reported (59). The resulting material is porous but can be improved by hot pressing.

F-3.5 Hot Spraying

F-3.5.1 Properties

Densities over 90 percent are obtainable in plasma-sprayed ceramics, even in tantalum carbide (melting point 7020°F). Sprayed tungsten deposits equivalent in properties to cold pressed and sintered material are claimed by Singleton, et al. (60).

F-3.5.2 Configuration Control

Inherently, sprayed deposits will have the best dimensional accuracy at their interface with the tool (external or internal). Tungsten presents very difficult problems in fabrication by conventional means. For this reason, the plasma spray deposition of tungsten structures on removable

mandrels found early commercial use. Singleton, et al. (60) lists the process advantages as follows:

- a. No size limitation
- b. Wide range of shapes
- c. Uniform properties throughout a section
- d. Simple, low tooling cost

Similar considerations apply to ceramic structure deposition by hot spraying. Norton Company has flame-sprayed Al_2O_3 on a soluble form to produce large nose cones.

APPENDIX G
APPLICATION OF DISLOCATION THEORY
TO DEFORMATION PROCESSES

This appendix summarizes theoretical investigations now in progress on the application of dislocation theory to metal cutting¹ and forming. Processes involving plastic deformation of metals and alloys are discussed in relation to the roles played by the environment and by the characteristics of the energy supply. Of particular interest are the effects which environmental changes induce in materials by modifying the energy requirements. Because the understanding and the access to new analytical methods provided by the study can open new avenues in the search for new processes, the complete study will be released in a separate report. In that report the discussion will be broadened to include high-energy-rate forming (e. g., explosive forming), wear, and friction.

The investigation rests on the hypothesis that plastic deformation of crystalline bodies results from the motion of dislocations and from interactions originating from such motion. The principal factors involved in the processes under consideration are (1) elastic limit and/or yield stress, (2) strain and ultimate strength, and (3) strain rate and strain hardening. These factors are related to the environment and to the energy supply through a system of parameters, which in turn express the field effects on the dislocation mechanism. The parameters are either intensive or extensive. Under equilibrium conditions the incremental changes in an intensive parameter will produce corresponding changes in the extensive parameters according to the equation

$$(de_j) = (c_{j,k})(di_k)$$

¹Metal cutting is included in the discussion because the deformation process in the shear zone is of interest.

where (de_j) is a column matrix of changes in extensive parameters, (di_k) is a column matrix of changes in intensive parameters, and $(c_{j,k})$ is a matrix of compliances. Alternatively, of course, the interactions can be defined by

$$(di_k) = (R_{k,j})(dc_j)$$

where $(R_{k,j}) = (c_{j,k})^{-1}$ is the rigidity matrix. Modifications of the environment or of the energy supply are reflected by changes in $(c_{j,k})$ (or, equivalently, $(R_{k,j})$).

The structure of the compliance matrix $c_{j,k}$ reveals such properties of the material as the following:

- i) Vectorial properties - (pyroelectricity and pyromagnetism)
- ii) Scalar-tensor effects (thermal expansion)
- iii) Vector-tensor effects (dielectric permittivity)
- iv) Tensor-tensor effects (electrostriction).

Second order effects usually introduce tensors of rank two or higher. (Consider, for example, the magnetocaloric effect in ferromagnetic materials near the Curie temperature.) When steady state properties are considered, they are correlated by a matrix equation of the type

$$(J_\alpha) = (-C_{\alpha,\beta})(\nabla\varphi_\beta)$$

where (J_α) is a flux vector, $(\nabla\varphi_\beta)$ is the gradient of the potential vector φ_β , and the matrix elements $C_{\alpha,\beta}$ are material constants called conductancies. The inverse elements $C_{\alpha,\beta}^{-1} = \rho_{\beta,\alpha}$ are resistivities.

The conductancies and resistivities are tensor quantities forming tensors of rank two and the products between these and the gradients are dot (scalar) products. The tensors of this type occur in connection with heat flow, thermoelectricity, Hall effect, thermomagnetic and thermogalvanic effects and related phenomena.

In thermodynamically irreversible systems, the relationships between the parameters are not single valued (hysteresis presents an example). Therefore, elastic limit, strain, strain rate, etc., being of an essentially irreversible nature, can not be defined in terms of compliances, rigidities, conductancies and resistivities. It is possible, however, to assess the effects of dislocations on the equilibrium and steady-state properties. Conversely, by manipulating either the intensive or extensive parameters, dislocations can be caused by react according to their dependence on the property matrix.

G-1 Metal Cutting

In metal cutting, energy required to remove a unit volume of material depends, as is well known, on the effective, or dynamic, shear stress and the shear strain. Energy consumed at the chip-tool interface usually represents only a small fraction of the total energy input. The energy consumption is reduced by reducing either the dynamic shear stress, the shear strain, or the frictional forces along the tool-chip interface.

G-1.1 The Nature of the Dynamic Shear Stress

Chip formation in the zone ahead of the tool edge can occur either by plastic deformation or by fracture. Plastic deformation is observed in face-centered cubic (fcc) metals at all temperatures and in body-centered cubic (bcc) metals above a certain critical temperature. Fracture is observed in brittle materials such as cast iron and in bcc metals below the critical or transition temperature.

In fcc metals, three stages are recognized in the stress-strain curve, as shown schematically in Figure G-1. Stage I is a linear region of small slope (the region of "easy glide"), Stage II is a linear work-hardening region of greater slope, and Stage III is an essentially parabolic region in which work-hardening is strongly temperature dependent.

Work-hardening results from interactions between dislocations. These interactions, which oppose dislocation movement, often take the form of jogs, a form of discontinuity which arises when two dislocations intersect. With

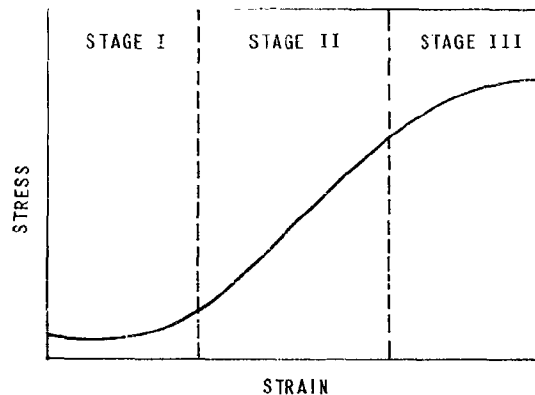


Figure G-1 SCHEMATIC STRESS-STRAIN CURVE FOR fcc METALS

increasing strain, the number of dislocations increases. Since the interactions then become increasingly numerous, it becomes increasingly difficult to produce further deformation. The classical mechanism by which the multiplication of dislocations is described is the Frank-Read source model. In this model a dislocation line anchored at two points is bowed outward by the applied stress until a critical line tension is exceeded. Beyond this point the loop expands spontaneously until opposite portions of the loop combine, whereupon the process repeats itself.

In fcc metals, the shear stress depends on the following parameters:

- a) Dislocation density
- b) Local absolute temperature
- c) Velocity of deformation
- d) Jog formation energy
- e) Elastic constants of the metal

Because of the rapid generation of loops from active Frank-Read sources, the third stage of work-hardening is established in the immediate vicinity of the

lower boundary of the stationary deformation zone. At large dislocation densities the interaction between dislocations becomes very pronounced, and considerable lengths of dislocations are annihilated. This mechanism competes with the annihilation of point defects and results in the net release of thermal energy. Heating of the deformation zone is quite significant and affects the elastic constants of the material. Therefore, the stress imposed on the zone reaches a level at which no further hardening occurs. Actually, the stress level decreases as the upper boundary of the deformation zone is reached.

Since such a process should be independent of the detailed mechanisms taking place in any particular elementary neighborhood, the stress-temperature curve exhibits essentially a linear relationship for pure metals, the slope depending on the strain rate.

Addition of impurities of appropriate size or of clusters of impurities introduces obstacles to dislocation motion. In this case the back stress tends to deactivate the Frank-Read sources, or increase the critical shear stress on the source so that the dynamic shear stress shows less temperature dependence. The net effect of such rise in the shear stress is the reduction of the macroscopic shear strain. The resultant heating is about the same, but the microscopic mechanism for the energy conversion is much more complicated and even less understood than in the case of pure metals.

Reasonably detailed numerical calculations show that there are very few side effects which can be effectively used to reduce the shear stress in fcc metals by a technologically significant amount. The case of bcc metals and alloys is much more complex. In general the role of precipitates and of long and short-range ordering has to be taken into account. In quenched solutions the impurity atoms can be assumed to be randomly distributed in the lattice. Their differences in size produce stresses which are directly proportional to the local expansion and inversely proportional to the cube of the distance. Such stresses produce two kinds of action on a dislocation line. The merit of the present theory depends greatly upon the detailed analysis of each individual case.

G-1.2 An Interesting Mechanism

It is interesting to note that in ferromagnetic materials the presence of dislocations influences such structure-sensitive magnetic properties as permeability, coercive force, and hysteresis loss. The effect of dislocations on coercive force and permeability can be tentatively explained in terms of the interaction between dislocations and the two-dimensional boundaries between adjacent ferromagnetic domains magnetized in different directions. The boundaries, known as Bloch walls, constitute a transition layer a few hundred lattice constants thick, in which the direction of magnetization gradually changes from one orientation to the other. Dislocations anchor the Bloch walls to a certain extent. When a magnetic field is applied which favors the growth of one domain at the expense of the other, the Bloch walls are not displaced as a whole but only bulge out between the anchoring dislocations. At a certain critical field strength (analogous to the critical line tension in the Frank-Read mechanism), the wall is released from its anchoring dislocations in a mechanism known as a Barkhausen jump. The critical field strength H_c depends on the dislocation spacing ℓ according to the formula

$$H_c = \frac{\alpha}{\mu_0} \frac{\gamma}{\ell M}$$

where γ is the wall surface energy, M is the magnitude of saturation magnetization in both domains, μ_0 is the vacuum permeability, and α is a numerical factor, about 3.

Now the exact nature of the interaction between dislocations and Bloch walls is not known. It is presumably of magnetic rather than elastic nature. The enforced displacements of the Bloch walls exert a drag on the dislocation. If these are piled up due to the obstacles, the back stress tends to shut off Frank-Read sources. We postulate that by superposition of a modulated magnetic field, which in metal cutting needs to be concentrated only in the cutting region, dislocation mobility can be enhanced, thereby producing a reduction in the shear stress, and thus making chip formation easier. The effect may be of significance especially for the machining of ultra-high strength ferromagnetic alloys.

G-1.3 Brittle Fracture in the Shear Zone

Although there is a dearth of data on cutting energy for materials which possess low-temperature embrittlement, it is expected that brittle machining requires less specific cutting energy. Work is in progress at the University of Illinois on a brittle machining theory based on the cleavage processes. Preliminary analysis shows that such a mechanism, when applied in metal cutting, is operative in the pulsing effect of the cutting tool. If the conjecture is valid, then significant reduction of the cutting energy is to be expected when the tool oscillates at approximately 3000 - 5000 cps. Whether this phenomenon has any relationship to the reported Fitzgerald effect is not yet known. Consideration of the influence of dislocations already present in the material shows that these have very little effect on the propagation of the crack, even in previously work-hardened material. The oscillatory effect essentially inhibits plastic relaxation when the hydrostatic component of the stress tensor is quite large. This is, of course, the case in metal cutting. It is, therefore, expected that a flaking type of chip would be produced, similar to the "type one" chip described by Ernst and Merchant.

For reasons noted above, the shearing stress in the brittle machining operation is practically independent of the initial dislocation density. A similar conclusion has been reached analytically for ductile chip formation and has been confirmed experimentally in copper and aluminum.

G-2 Forming

If a material is prone to brittle fracture at moderate strains and retains this property to higher temperature, it cannot be formed plastically by any known conventional means. The viewpoint adopted in this investigation is to seek those dislocation interactions which permit a large amount of plastic flow but which, at the same time, inhibit fracture.

For cold-working operations, the limiting factor is the strain at which, due to prior work-hardening, the stress reaches the fracture level. In this case the arguments are based on Stroh's concept that the stresses from a pile-up of dislocations can crack the material in the immediate vicinity of the pile-up.

Such cracks once formed will grow in a brittle manner provided that the Griffith condition for crack propagation is satisfied and that there is no plastic relaxation around its apex to halt its propagation.

It is well known that microstructure and other metallurgical parameters influence the formability of materials. These factors influence the deformation process within the bulk of the metal, but they also have a very important influence on the boundary conditions. The extent of such influence depends, of course, on the type of lubricant used and the surface properties of the forming tool.

G-2.1 The Flow Stress in Forming

In cold work, the shape of the stress-strain curve and the rate of straining are of fundamental importance. The relation of the flow stress to dislocation mechanisms is not understood well enough to identify treatments capable of lowering the workhardening coefficient for many important materials. For ferromagnetic materials the utilization of strong magnetic flux, as described earlier, may offer some benefits.

There are, however, some general ideas regarding the flow stress, which are applicable to the forming process:

a) In the case of quenched solid solutions, as has already been mentioned with regard to metal cutting, impurity atoms can be assumed to be randomly distributed in the crystalline lattice. The impurity atoms near the dislocation line exert on it oscillating stresses. These oscillating stresses, of zero mean value, have a wavelength equal to the average distance between the atoms and an amplitude proportional to the size factor of the impurity. Impurity atoms on the dislocation line interact strongly with it to produce a zigzagging dislocation line. Under the applied stress, the dislocation line moves piece by piece, leaving one solute atom after another. It continues its zigzagging course because the neighboring atom replaces the one just abandoned. It is expected that there exists a critical temperature below which the flow stress rises sharply with lowering temperature. Above this critical

temperature, thermal vibrations are large enough to produce jumps from atom to atom under a stress sufficiently large to overcome the long-range interactions with the dislocation network.

b) Age-hardening solutions have a stress-strain curve which exhibits the classical yield-point phenomenon. This fact suggests that the impurities are attracted to the immediate vicinity of the dislocation. The net effect, in this case, is that the starting of the glide is more difficult than its continuation.

If means can be devised by which the locking by impurities can be reduced, the initial value of the flow stress can be reduced. High-frequency pulsing, e.g., as noted in Section G-1.2, at low temperature may provide such a technique because it is advantageous to keep quenched solutions dispersed. This method is somewhat difficult to apply, however, because at high strain rates the brittle-ductile transition temperature is quite high, and age hardening can readily occur.

G-2.2 Structural Phenomena at Large Strains

Strains in industrial forming processes are large. After the initial flow stress has been reached, grain boundaries prevent any large amount of easy glide. Coherence between grains is maintained by several plastic mechanisms simultaneously acting in each grain, i.e., the activity embraces several slip systems, or slip plus twinning or martensitic transformation. Because of the interactions between grains, bending movements appear in many grains even when applied stress is in tension or shear. These movements are usually relieved by kink band, i.e., by plastic relaxation. If this relaxation is not sufficient, cracks will appear at the grain boundaries.

In the case of fcc metals, rapid build-up of Cottrell barriers is a consequence of the simultaneous action of several glide planes. These barriers, which are formed by the combining of two dislocations and their subsequent dissociation into relatively immobile partial dislocations, produce a locking effect. As a consequence, the linear Stage II and the

parabolic Stage III of the stress-strain curve (Figure G-1) are observed immediately. The linear stage is quite noticeable at low temperatures, and the hardening rate is obtained by averaging the applied stress over various active slip systems. The parabolic stage onset stress decreases rapidly with increasing temperature.

APPENDIX H
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Studies were continued within the framework of process elements established at the outset of the project and reported in the first interim report.

Highlights are: (1) the concept of "embrittlement mechanisms" based on one or more of several material embrittlement mechanisms discussed in the report and (2) recommendations for experimental investigation of surface hardening, oxidation retardation, and embrittlement of materials by ion bombardment.

A summary of theoretical investigations, still in progress, on the application of dislocation theory to metal cutting and forming is included. An approach to process synthesis is outlined and related to immediate and long-range Air Force needs.

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