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FINAL REPORT

on

AMORPHOUS AND METASTABLE MATERIALS
(Report No. A-4744, Task No. 72)

by

Robert E. Maringer

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September 1976

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FOREWORD

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AMORPHOUS AND METASTABLE MATERIALS

by

Robert E. Maringer

INTRODUCTION

The purpose of this report is to discuss the relatively new and rapidly expanding field of amorphous metals, with special emphasis on the potential applicability of these new materials to DoD needs. It is apparent, on examining this field, that the same methods used to produce amorphous metals will also produce crystalline materials of very unusual crystal structures or with very unusual mechanical, chemical, or physical properties. Therefore, the discussion will include this surrounding technology, under the general term "metastable materials".

In the preparation of this report I have sought to use my own background, to read and absorb as much as possible from the numerous review articles, to search the newer literature (mostly 1972 to the present), and to contact personally many of the most active workers in the field. The personal contacts were used to try to get a general impression from those interviewed about the future of the field, any factors which might be inhibiting the growth of the field, and what (if anything) the DoD might do to assist in exploiting the field.

The names and affiliations of researchers contacted are given in Appendix A. Their comments and thoughts are integrated with my own in the following discussion. For the most part, no individual credits are given. This is partly because many of the ideas discussed were expressed by each of several individuals, and partly because such detailed referencing would interfere with what I hope to be a short, readable report.

The enthusiasm expressed herein for the almost unprecedented potential inherent in the field of metastable materials reflects not only my own feelings, but, I believe, those of most or all of those actively engaged in research on this new frontier of materials science. This is easily documented in the literature. Cotterill^{(1)*}, of the Technical University of Denmark, refers to metallic glasses as "a new class of materials". Cahn⁽²⁾ of the University of Sussex says "a complete new metallurgy has been created". In the announcement of a forthcoming

*References are given at the end of the report.

meeting on noncrystalline solids (Materials Research Society, Cambridge, Massachusetts, November 15-17, 1976) it was stated: "Major new advances in technique have made a whole new universe of materials--the noncrystalline phase-- available". These are not exaggerations. These are the considered opinions of highly qualified scientists based on some of the remarkable experimental results which have emerged from research laboratories throughout the world in less than two decades.

BACKGROUND

The whole field of what we will call "metastable materials" was spawned by Duwez and his students at the California Institute of Technology and by Salli and his co-workers in the U.S.S.R. in the late 1950's. Duwez published the first description of an amorphous metal in 1960⁽³⁾, and has since been correctly identified as the "father" of the field. The first "metallic glass", a gold-silicon alloy, was produced from the melt by very rapid quenching ($\sim 10^6$ C per second).

In the amorphous state, metals take on entirely new characteristics. Their mechanical, physical, and chemical properties all seem to change relative to their crystalline counterparts. However, this is only one of four distinct effects that rapid quenching can have. These are:

- (1) *Supersaturation.* Primary solid solutions can be extended to higher solute contents. This introduces totally different capabilities for the production of unusual solid-solution hardening, or for the production of new age-hardenable alloys, or for the production of very homogeneous structures. It also suggests the possibility of exerting a significant degree of control over electron/atom ratios and over lattice parameters.
- (2) *Formation of intermediate compounds and crystal structures.* These introduce the capability for the production of new and different alloys.
- (3) *Grain-size control.* Rapid quenching, in particular, generally produces a fine grain size which becomes still finer as the quench rate increases. As grain sizes decrease below, perhaps, 5 microns, various mechanical properties become strongly affected. These controllable grain sizes open up whole new approaches to powder metallurgy and to the exploitation of superplasticity.

- (4) *Amorphousness*. In this state the crystal formation is totally suppressed (no long-range order) and a new class of materials is formed.

One or more of the above effects may be observed in materials as the quench rate from the liquid state increases beyond 10^4 C per second or so. However, liquid quenching is only one of a number of methods capable of producing such effects. In general, when atoms or molecules are assembled into the solid state from some precursor state (vapor, liquid, solid, or from solution or suspension) at an appropriate rate and temperature, the mobility of the individual particles can be sufficiently decreased to suppress the formation of equilibrium structures. These, then, are the "metastable materials" under discussion. In addition to rapid quenching from the liquid state, a variety of other methods may be appropriate. These include:

- Vapor deposition
- Sputtering
- Plasma spraying
- Electrolytic deposition
- Electroless deposition
- Ion implantation
- Neutron irradiation
- Shock

Research in this country and abroad has concentrated heavily on quenching from the liquid state as a means of producing metastable materials. There are probably several reasons for this--novelty being one. A big attraction of the rapid quenching is the speed and efficiency of many of the quenching methods. For those who envision commercial markets, speed and efficiency are vital. It is pertinent, therefore, to discuss liquid quenching in more detail so that the reader can gain some feel for the capabilities and limitations of the method.

Methods of Liquid Quenching

There are almost as many variants to the techniques of liquid quenching as there are researchers. Duwez developed a gun technique, and used a sudden

burst of gas to propel a small droplet of molten metal onto a chilled (usually moving) substrate (usually copper). This resulted in a small splat of solid metal which was quenched at rates in excess of 10^5 C per second. This also resulted in the generally accepted terms of "splat cooling" or "splat quenching". The splats or foils produced are somewhat irregular in size, shape, and thickness. The thinner sections generally represent the more rapidly quenched portions of the foil. Such foils are easily studied by X-ray and electron microscope techniques and are often large enough to prepare specimens suitable to mechanical or electrical property testing. As a result, laboratories throughout the world have picked up the generalized method and added their own changes. These variants involve the way the metal charge is melted, the way the molten droplet is supplied to the substrate, and the way the substrate is designed to receive the droplet. One example of such a variant is the device developed by Davies and Hull⁽⁴⁾ as shown in Figure 1. This device causes a gas-propelled droplet of molten metal to impact upon a "ski slope" shaped cooled substrate. This produces an elongated splat of about 10 x 20 mm, with an average thickness of less than 20 μ m. The authors estimate that they achieve cooling rates of up to 10^{10} C per second.

While the methods for producing these splat-cooled foils are very important and useful from a research point of view, they are very limited from a production point of view. Industrial interest in metastable materials centers more on filament, ribbon, or sheet forms. (Powders will be discussed later.) Fortunately, some alternative methods are available which appear to have the appropriate qualities to permit both rapid quenching and high productivity, and to provide continuous products as well.

The oldest of these is called "melt spinning". In its simplest form, free-flight melt spinning, a stable jet is created by forcing molten metal through a small orifice under pressure (see Figure 2). The liquid jet is then caused to solidify in flight, sometimes through the use of gaseous aerosol or liquid quenching media to enhance the cooling rates. Free-flight melt spinning produces continuous round wire. The method was first developed before the turn of the century⁽⁵⁾, was subsequently developed by Pond⁽⁶⁾, and later improved upon by researchers at the Allied Chemical Corporation⁽⁷⁾. Both Monsanto Corporation⁽⁸⁾ in the U. S. and Michelin⁽⁹⁾ in France have had extensive programs (thus far unsuccessful) to utilize this method for the production of tire cord. Quench

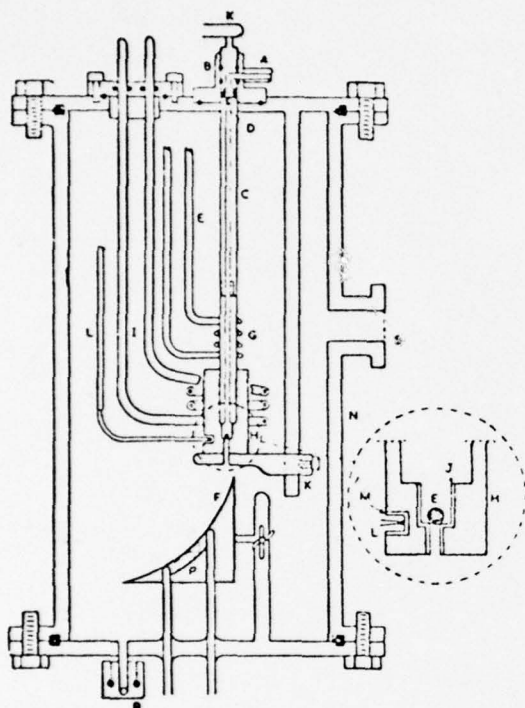


FIGURE 1. DIAGRAM OF APPARATUS FOR SPLAT-QUENCHING IN SEALED INERT ATMOSPHERE

Key to parts: A, high-pressure gas inlet; B, high-pressure chamber; C, shock tube; D, Mylar diaphragm; E, molten sample; F, "ski slope" surface; G, cooling coil; H, graphite crucible; I, r.f. heating coil; J, alumina lining for sample chamber and orifice; K, clamp; L, Pt-Pt-Rh thermocouple; M, alumina lining for thermocouple well; N, steel chamber; P, cooling for quenching surface - water or liquid nitrogen; R, pressure-release valve; S, port for diffusion pump and inert gas supply.

[From Davies and Hull(4)]

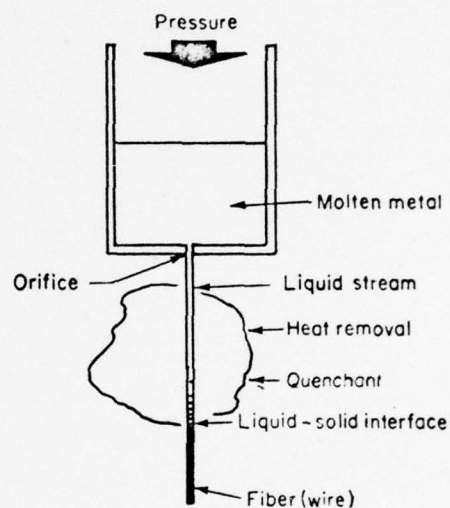


FIGURE 2. SCHEMATIC DRAWING OF THE FREE-FLIGHT MELT-SPINNING PROCESS

[From Pond, et al.(6)]

rates are limited in free-flight melt spinning because of the relatively low heat-transfer rates which are readily achievable. However, a simple variant of the process avoids this difficulty.

In chill-block melt spinning, the metal jet, created as above, impinges on a chilled, rapidly moving surface (see Figure 3). The liquid jet flattens into a ribbon shape, solidifies, then spontaneously releases as a continuous ribbon product. The direct contact of the molten metal with the cooled substrate greatly enhances the quench rate. Again, this method was developed by Pond⁽⁶⁾ and improved by workers at Allied Chemical Corporation⁽¹⁰⁾ and elsewhere⁽¹¹⁾. The method is so simple and effective that it has been adopted by laboratories around the world to produce metastable materials for further study. Ribbons produced by chill-block melt spinning will normally have thicknesses of from less than 10 to several hundred microns and widths of from less than one to several millimeters. Quench rates can exceed 10^7 C per second. Quenching on the inside surface of a rotating cylinder enhances the quench rate by utilizing centrifugal force to maintain contact between the casting and the substrate for longer times.

Chen and Miller⁽¹²⁾ developed a system which involves introducing a droplet of metal into the bite of two contra rotating rollers (see Figure 4). This produces a foil quenched from both sides, but with the time of contact between the sample and the chilled substrate being very limited. Babic, et al.⁽¹³⁾, in Yugoslavia, at about the same time, combined the technique of melt spinning with that of the double roller and synchronized the flow of liquid metal into the bite with the speed of the rollers. They claimed that this has the potential to produce continuous ribbon or strip.

The melt-extraction process developed at Battelle⁽¹⁴⁾ involves bringing the edge of a spinning disk into contact with a source of molten metal. The source can be contained in a crucible (Figure 5) or as a pendant drop (Figure 6). The molten metal solidifies on the disk edge, and is subsequently thrown off as a filament or as a staple fiber.

These latter three methods have great potential for a scale-up, and indeed, melt spinning and melt extraction are already in limited commercial production. Each of the methods has its virtues and its faults. They are deceptively simple. The melt-spinning methods (and probably the twin-roller

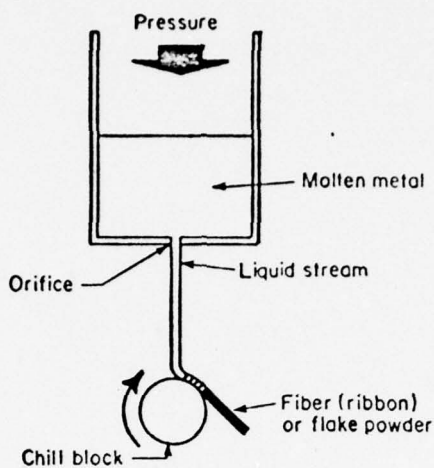


FIGURE 3. SCHEMATIC DRAWING OF THE CHILL-BLOCK MELT-SPINNING PROCESS
[From Pond, et al. (6)]

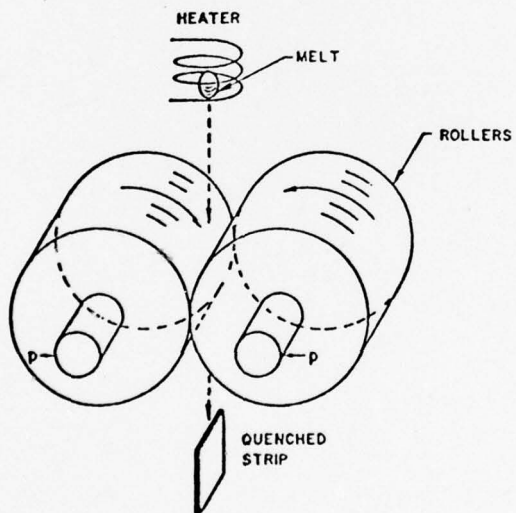


FIGURE 4. SCHEMATIC DRAWING OF THE QUENCHING APPARATUS

Rollers are 5-cm diam x 5-cm width and held together with pressure, p , which ranges from 20 to 90 kg. The rotation speed of rollers, ω , can be varied from 100 to 5000 rpm.

[From Chen and Miller (12)]

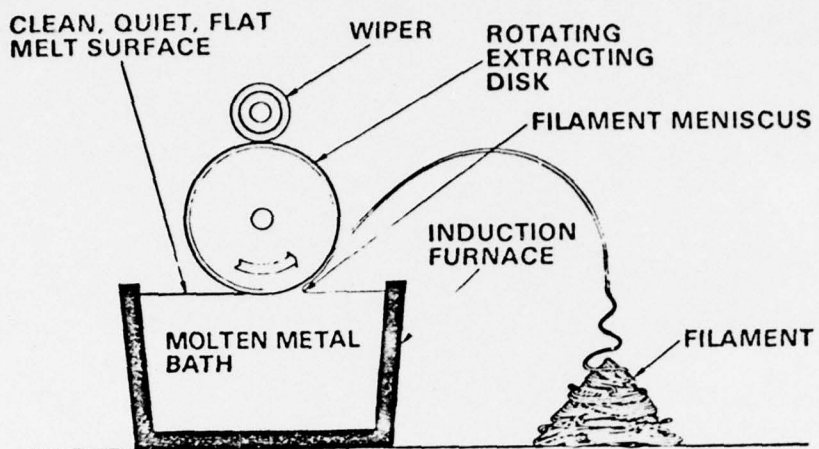


FIGURE 5. ILLUSTRATION OF THE PRINCIPLES OF CRUCIBLE-MELT EXTRACTION

[From Pond, et al.⁽⁶⁾]

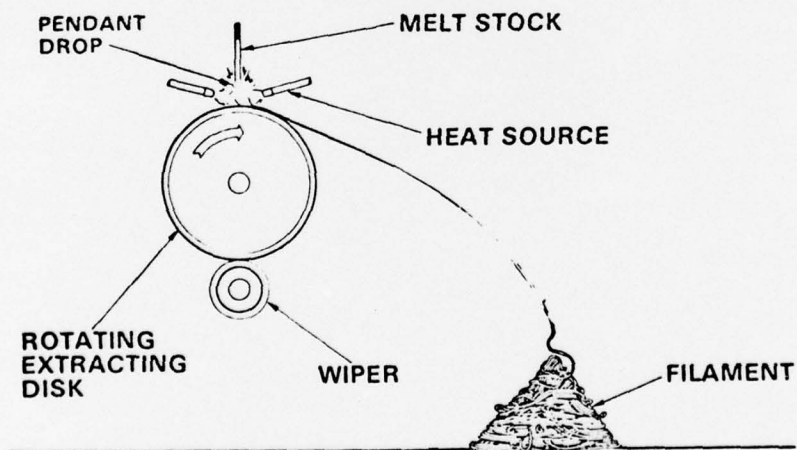


FIGURE 6. SCHEMATIC DRAWING OF PENDANT-DROP-MELT EXTRACTION

[From Pond, et al.⁽⁶⁾]

method as well) require a crucible and an orifice. Materials compatibility problems can be very serious when it comes to long-term operations or the spinning of high-melting-point or reactive materials such as B or Ti. However, the control of the liquid flow relative to the quenchant or to the substrate enables one to exert excellent control on product dimensions. The impact of the jet onto a substrate assures good thermal contact and increases the quench rate, especially if the casting is done on the inside surface of a rotating drum. Melt extraction, on the other hand, has no orifice (and in one modification, no crucible) which greatly minimizes materials compatibility problems. However, quench rates are somewhat lower than those of melt spinning unless unusual methods are used to enhance the quench rates. Twin-roll techniques quench from both sides of the ribbon at once, but demand great precision in roll performance and are limited by the very geometry of the system to a very short (but very effective) time of thermal contact between the casting and its substrate.

Still another method for rapid quenching involves rapidly heating a very thin surface layer of an alloy by an external heat source, then allowing the layer to freeze rapidly. Usually the heat source is a laser beam. Recent work⁽¹⁵⁾ by Kear and Breinan shows that this is an industrially promising technique which could "glaze" specific parts with an amorphous layer to take advantage of some of the unique properties of amorphous materials while still maintaining a more-or-less conventional chemistry in the remaining bulk of the part.

The techniques described above will produce a wide variety of material--powder, ribbon, wire, staple fiber--all of rather limited dimensions (other than length). The thickness is limited to probably less than a few hundred microns by heat-transfer considerations. The freshly cast material itself limits the heat flow so that rapid quenching is not readily achieved on thicker samples. Ribbon widths are currently limited to a few millimeters. A real need exists for wider strip or sheet⁽¹⁶⁾, but the manufacture of this by direct casting is not yet in the state of the art. In view of the rapid progress in techniques made over the last decade, however, it does not appear to the writer that this is an intractable problem. I have heard privately, in fact, that Allied Chemical Company is now capable of casting 4-inch-wide strips of amorphous material.

In most of the rapid-quenching processes which appear capable of continuous production, (i.e., melt spinning, melt extraction, double-roller casting) the quenching process takes place in two stages. Primary quenching occurs when the casting is in thermal contact with the substrate. Due to shrinkage and other forces, the casting breaks the bond between itself and the substrate. Subsequent cooling can be referred to as secondary quenching.

In general, primary quenching attains the highest rates. However, the forces that tend to break the good thermal contact between the casting and the substrate are such that, unless artificially enhanced, the contact is disrupted in very short times, usually milliseconds or less. Various approaches to maintain this contact, and thus to enhance primary quenching, have been advanced (e.g., rougher surfaces to increase contact area and bond strength, gas pressure or mechanical rollers to counter the release forces, spinning on the inside of a drum to enlist centrifugal force to maintain contact). Other approaches have been used to enhance the secondary quench rates (e.g., directing product immediately into a gaseous or liquid medium, going directly into a secondary pinch roller system).

Both primary and secondary quenching are important in the manufacture of all forms of metastable materials, since grain growth or crystallization can occur rapidly enough during secondary quenching to completely destroy any structures produced during primary quenching. There are hints in the literature that methods exist to enhance both primary and secondary quenching, but there is little evidence to suggest that these are being pursued.

For example, Schile^(17,18) uses electrostatics to cause particles of coolant to be directed at a liquid jet as created by free-flight melt spinning. The particles may, in fact, be such that they form an alloy surface on the filament while at the same time enhancing the quenching rate. This same general procedure could be used to enhance secondary quenching for chill-block melt spinning, melt extraction, or the double-roll technique. Ditto⁽¹⁹⁾ reports that the use of a magnetic field enhances the rate of cooling of free-flight melt-spun filament, but the mechanism is not known. Unpublished research from the Mead Corporation⁽²⁰⁾ shows that an electrostatic field appears to significantly enhance the solidification rate of a jet of molten cast iron. A Japanese report⁽²¹⁾ documents an increase in the rate of heat transfer upon the imposition

of an electrostatic field. Soviet reports indicate an increase in the range of supercooling as a result of an imposed electrostatic field⁽²²⁾ as well as an influence of such a field on the crystallization of vapor-deposited films^(23,24). Richardson⁽²⁵⁾ reports a direct effect of a field on liquid-metal surface tension. It is clear, I think, from the above, that the methods of rapid quenching to achieve the metastable state are still in an evolutionary stage. Much remains to be done, both in developing and understanding of the fundamental process of solidification at these high quench rates and in developing the manufacturing technology which will permit the efficient production of these materials on an industrial scale if the anticipated markets develop.

Alternative Methods

Most of the alternative methods for the production of amorphous or other metastable materials, and these include the aforementioned vapor deposition, sputtering, plasma spraying, electrodeposition, electroless deposition, etc., are particularly applicable to the formation of a thin film on a suitable substrate. In some cases, the thickness can be built appreciably, thus allowing the preparation of more massive materials. A particularly exciting development by Giessen, et al.⁽²⁶⁾, is the production of amorphous Cu-40Zn over 0.7 mm thick by a plasma-arc-spraying technique. In general, however, these methods are slow, and the products have a somewhat different character from those produced by quenching⁽²⁷⁾.

There is at least one technique, the so-called Schladitz process⁽²⁸⁾, which produces fibers as small as 0.1 μm in diameter (and up to several millimeters in length) by vapor deposition from iron or nickel carbonyls under the influence of a magnetic field. Research on this unique process is underway at the University of Virginia. Wawner⁽²⁹⁾ reports grain sizes as small as 50 to 200 \AA . It is not yet clear how much of an overlap exists in the comparative advantages (or disadvantages) of deposition techniques relative to quenching techniques. This is an area toward which more attention should be directed.

It has been reported that Pd-Si alloys can be rendered amorphous through neutron irradiation⁽³⁰⁾ and that ion implantation induces amorphousness⁽³¹⁾. Both of these techniques have severe limitations, but should be further explored to evaluate their potential usefulness. Amorphous materials

produced by shock have been reported in meteorites⁽³²⁾. Here again is a method with unknown potential.

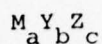
Powder Metallurgy

It has recently become apparent⁽³³⁾ that the behavior of powdered metals in subsequent processing depends to a large extent upon the way the powders were prepared. In particular, very fine particles can be sintered into dense solids at much lower temperatures. Further, fine grain sizes, even though the particles themselves are relatively large, also affect subsequent processing and subsequent properties. The methods used to prepare such powders are, in fact, directly related to those described above to produce metastable materials. Most of these are, again, high-quench-rate techniques. German⁽³⁴⁾ and English⁽³⁵⁾ workers are using a spinning-cup technique to throw molten metal droplets against cooled substrates. Researchers at Pratt & Whitney⁽³⁶⁾ are using a similar technique but cooling the droplets in a blast of gas. Swedish workers⁽³⁷⁾ are using an ultrasonic shock wave to break up a stream of liquid metal into very fine particles (which cool faster). Soviet scientists⁽³⁸⁾ are creating ultrafine (20 to 50 Å) powders by the reduction of suitable oxides in a plasma field. Other Soviet work⁽³⁹⁾ shows that, if the particles become small enough, they become amorphous. The techniques to make amorphous or microcrystalline flake now exist in the laboratory⁽⁴⁰⁾.

Much of the work on powder products is already in the prototype manufacturing technology stage. Once again, much remains to be done, but the potential applicability of these new materials and materials technologies is awesome, and very close at hand.

Amorphous Compositions

By now some hundreds, perhaps thousands of different alloys have been rapidly quenched into the amorphous state. Their diversity is indicated (and somewhat organized) in a patent recently issued to the Allied Chemical Corporation⁽⁴¹⁾. They claim amorphous or partly amorphous alloys can be made from an alloy of the formula



where

M is Fe, Ni, Cr, Co, and/or V

Y is P, C, and/or B

Z is Al, Si, Sn, Sb, Ge, In, and/or Be

a = 60 to 90 atomic percent

b = 10 to 30 atomic percent

c = 0.1 to 15 atomic percent.

The number of permutations of these alloys is enormous, yet those do not nearly exhaust the possibilities. A more general picture of the binary systems from which amorphous metals might be formed by liquid quenching has been discussed by Collings, et al.⁽⁴²⁾ These include:

- (1) Rare-earth metals alloyed with late-transition metals (Group VIII of the periodic table), e.g., Gd-Co
- (2) Early-transition metals (Group III through IV) alloyed with late-transition metals, e.g., Zr-Co
- (3) Late transition metals alloyed with metalloids, e.g., Co-P
- (4) Metalloids alloyed with noble metals, e.g., Au-Si
- (5) Noble metals alloyed with early-transition metals, e.g., Cu-Zr.

There is, therefore, no shortage of potential amorphous alloys. At this time, only a small fraction of these alloys have been produced, and significant property information is available on fewer still. There appear to be virtually no limitations at all on candidate materials for the crystalline metastable technology. Even materials which are already glassy show differences when prepared by rapid quenching⁽⁴³⁾ to the extent that Roy⁽⁴⁴⁾ proposes different classes of glasses.

Properties of Metastable Materials

The properties of metastable materials depend upon which of the effects cited earlier (supersaturation, novel crystal structures or compounds, grain size, and amorphousness) are brought into play by the combination of alloy composition and processing. The spectrum of property changes are so vast that it is difficult to do justice to them in a short report. It may serve the purpose to simply cover in the barest detail some of what I consider to be the most exciting and potentially the most useful observations reported. The observations on crystalline metastable materials are considered first.

Beghi, et al.⁽⁴⁵⁾, in Italy reported 600 percent elongation in a splat-cooled foil of Al-17 w/o Cu alloy. This affirms the supposition that the fine grain size produced by splat cooling can result in superplastic behavior.

Toda and Maddin⁽⁴⁶⁾ reported a sixfold increase in the yield strength of a rapidly solidified Al-5 w/o Au alloy.

Varich, et al.⁽⁴⁷⁾, in the U.S.S.R. reported that the hardness of an Al-Zr alloy increased with the temperature from which the alloy was liquid quenched.

Ramachandrarao and Anantharaman⁽⁴⁸⁾ in India reported that different metastable crystal structures were produced from the same alloy, depending upon the temperature from which the alloy was liquid quenched.

Lebo and Grant⁽⁴⁹⁾ observed increases in the yield strength and the tensile strength, as well as a sevenfold increase in the fatigue strength of 2024 aluminum made from splat-cooled powder.

Durand, et al.⁽⁵⁰⁾, observed intense and rapid age hardening at 20 C in 7075 aluminum alloys prepared from splat-cooled powder.

Faninger⁽³⁴⁾ in Germany reported improved corrosion resistance in Al-Fe alloys prepared from splat-cooled powder.

Kaufmann⁽⁵¹⁻⁵³⁾ reported dispersion-hardened Ni-, Zr-, and U-based alloys by precipitating highly insoluble metals from the splat-cooled alloys.

Luo, et al.⁽⁵⁴⁾, reported that splat-cooled AuGe is superconducting, but elemental Au and Ge are not.

Wang, et al.⁽⁵⁵⁾, reported that polyethylene sheet was made tougher by rapid quenching.

Any number of other observations could be added to this list, but it is preferable to go on to present similar citations of observations made on amorphous metals.

Tsuei⁽⁵⁶⁾ reported that a splat-cooled $\text{Te}_{70}\text{Cu}_{25}\text{Au}_5$ metallic glass is semiconducting. He also showed that the thermoelectric power of this metallic glass was about 50 times that of the same alloy in the crystalline state.

Willens, et al.⁽⁵⁷⁾, demonstrated an inductance thermometer of metallic glass with a temperature resolution greater than 1 mdeg.

Goldstein⁽⁵⁸⁾ has used metallic glasses as microprobe standards because of their superior chemical homogeneity.

Tsuei and Duwez⁽⁵⁹⁾ have reported a resistance thermometer of amorphous $\text{Cr}_7\text{Pd}_{73}\text{Si}_{20}$ which is not only very sensitive to low temperatures, but the resistivity is unaffected by relatively heavy doses of neutron irradiation. Of equal interest, Lesueur⁽³⁰⁾ reports that Pd-Si alloys can be made amorphous from the crystalline state by radiation.

Krishnanand and Cahn⁽⁶⁰⁾ have observed that metallic glasses can be rolled to 30 percent reduction, recovered by annealing, and rerolled.

Diegle and Slater⁽⁶¹⁾ have reported that there are significant electrochemical differences between metallic glasses and their compositional equivalent in crystalline form.

Masumoto and Maddin⁽⁶²⁾ observed that metallic glasses have high toughness as well as high strength. Gilman⁽⁶³⁾ expects tensile strengths of metallic glasses to exceed 375 ksi.

Kikuchi, et al.⁽⁶⁴⁾, in Japan reported Fe-Co based metallic glasses to have exceptionally low magnetic coercivity, and attributed this to near zero magnetostriction and the isotropic nature of the amorphous material.

Dutoit and Chen⁽⁶⁵⁾ observed unusually low acoustic attenuation in metallic glasses.

Kear and Breinan⁽¹⁵⁾ have produced amorphous skins on suitable alloys by melting a thin surface layer using a laser, and permitting the layer to freeze rapidly.

Galasso, et al.⁽⁶⁶⁾, prepared amorphous boron alloys by splat-cooling techniques.

Spear, et al. ⁽⁶⁷⁾, in England report the first successful p-n junction formed in amorphous silicon produced by the glow-discharge decomposition of silane mixed with trace amounts of donor or acceptor impurities. Holmes-Siedle ⁽⁶⁸⁾, commenting on the development states that "a new device technology may be in the making" which could lead to integrated circuits "as large as the page on which this is written".

These and other properties have been reported which reinforce the excitement of those actively engaged in research and development in the field. In effect, the materials scientist has been given the tools to add a whole new dimension to his studies. He can now control composition and structure to an extent never before possible.

There are some limitations, of course, and these must be borne in mind at all times. Amorphous metals exist in the glassy state only at relatively low temperatures. They will, on exposure to higher temperatures (several hundred degrees C, more or less, depending upon the alloy) crystallize and lose many or all of their attractive properties. Thus, metallic glasses are not and probably never will be candidates for high-temperature service. Moreover, metallic glasses usually have elastic modulus values 30 percent or so less than their crystalline counterparts, and they are usually less dense as well. These characteristics of metallic glasses will inhibit their use in some applications, but the limitations seem a small price to pay for the almost unbelievable freedom to control other properties.

The crystalline metastable materials may have some temperature limitations as well. As the very name "metastable" implies, these alloys will tend to revert to more equilibrium structures as the temperature rises. However, this very reversion is the source of much of the interest in these alloys, since it opens up great possibilities in precipitation hardening, with added control of both particle composition and spacing. In fact, such control is reported by Grant to permit even higher temperature usage for certain alloys.

As with any new materials, the metastable materials have strengths and weaknesses which will make them exceptionally suitable in some applications, and worthless in others. The suitable applications are so broad and potentially revolutionary that no apology need be made for the limitations which exist.

POSSIBLE DIRECTIONS FOR EXPLOITATION

Because the whole field of metastable materials is still in the frontier stage, speculation about its future development and applications is hazardous. It is a bit like trying to predict the ten dollar pocket calculator knowing only that semiconducting behavior has been observed. The very breadth of the observed property changes in metastable materials hints at the diversity of the potential. However, the attempt must be made at this point so that the reader can gain some insight into the future worth of this technology.

The speculations listed below fall into three categories: (1) new products made possible by the methodology being developed to produce metastable materials, but with metastability of the product playing no role, (2) polycrystalline metastable products, and (3) amorphous products.

Products of Methodology

A great deal of effort has been spent by many organizations to develop the means to rapidly quench materials in production quantities. These methods lend themselves to the production of wires, filaments, staple fibers, or powders of almost any metal, and of many nonmetals. Thus, it is now possible to manufacture many materials in forms that were not economic, or perhaps not even possible, in the past. Such products may or may not have an enhanced value because of metastability. For example, it is surprisingly easy to cast Hadfield steel (14 percent manganese steel) into filamentary form. This alloy is extremely difficult to draw, and is therefore expensive in wire form. Except as welding rod, it is not available in wire form. It could now be made available at low cost should a need develop. Some additional thoughts are presented below.

- Control of shape and size of particles can permit high green strength in powder compacts
- Casting of filaments with channels for use as wicking in heat pipes
- Casting of precursor fibers for subsequent extrusion to submicron-size fibers

- Casting of materials normally not available as fiber (B, Si, Al_2O_3 , TiAl, etc.) for composites or chemical or electrochemical applications
- Casting of fiber mats for armor or vibration absorption
- Generation of airborne radar-chaff
- Casting of tungsten carbide or other abrasive in staple fiber form to be incorporated with Cu or Co in tool bits
- Casting low-cost staple fiber to "rheocast" or "thixocast" into composite die castings
- Direct casting of nonwoven metal screening
- Use of submicron-size Schluditz fibers in conducting coatings (lightning suppression, etc.)
- Fibers for high-gradient magnetic-field separators.

Crystalline Metastable Products

As soon as one introduces some form of metastability (but not amorphousness) into the products, the potential includes most of the preceding list and takes on some products of a different character. The following list emphasizes those directions or applications which benefit from greater homogeneity, smaller grain size, and/or some degree of supersaturation.

- Whole new families of precipitation-hardening alloys (Be base, for example) resulting from ability to supersaturate
- Whole new families of materials with different crystal structures (β -stabilized Be, for example)
- Whole new families of solid-solution-strengthened alloys
- Prealloyed powders of all compositions leading to more efficient powder-metallurgy processing, superior bearing and tool steels, superior spray coatings, etc.
- Whole new series of alloys with controlled chemical and electrochemical applications (catalysis, batteries, fuel cells)

- Whole new series of alloys and material forms (sheet, in particular) capable of superplastic forming
- Tailormade burning rates and temperatures for flares, for reinforcement of solid rocket fuels
- Full control of particle size and grain size to minimize problems of toxicity, surface contamination, pyrophoricity, etc., in powder
- Superior hydrogen storage alloys
- Superior permanent magnets.

Amorphous Products

Once the materials produced become amorphous, the potential expands still further, incorporating most of the ideas previously listed, and including:

- Superior corrosion resistance, tailored to meet a specific environment
- Very high permeability ferromagnetic materials for use in transformers, switches, power-supply systems, inverter circuits - smaller, lighter, cheaper, lower power requirements
- Abrasion-resistant magnetic recording heads
- Bubble memory system for computers with storage capacity nearing that of the human brain
- Whole series of radiation-resistant switching devices microelectronic circuitry, microoptical circuitry
- Vapor deposition of p-n junctions, huge integrated circuits
- New superconducting, photovoltaic, thermoelectric, magnetostrictive devices.
- Thermal and electrical conducting substrates to suppress epitaxial growth
- Whole new families of composites
- New classes of permanent magnets

- New families of catalytic materials
- Radiation-resistant container for fusion reactor
- Prestressed composites.

It is important to recognize that, not only do metastable materials provide almost unlimited opportunities for new or improved products, but they do so in what appears at the present time to be a more efficient way. Specifically, the methods used to produce metastable materials are generally energy conservative. Direct casting to final dimensions, for example, eliminates most of the energy and capital-intensive steps of conventional manufacture. Metastable materials usually involve less material waste as well. A vapor-deposited p-n junction would involve only a layer some tens of microns thick, most of which would be functional. Conventional processing of a semiconducting chip wastes more than half of the material in cutting and etching alone, while the bulk of the remainder is required to permit handling and processing. Finally, many of the elements used in metastable materials (Si, S, P, etc.) are plentiful in the earth's crust and readily available. Thus the driving forces of economy, efficiency, and materials and energy conservation are potent motivations in the research and development of metastable materials.

METASTABLE MATERIALS AND DOD NEEDS

In looking at where metastable materials can contribute to DoD needs it is easy to look at an overall technology such as powder metallurgy and to predict that the introduction of the concepts of metastability into this art may produce components with better fatigue resistance, less material cost, less use of critical materials, better control of part-to-part uniformity, better corrosion resistance, better control of density, high strength at fractional densities, exceptional green strengths, superior forging and sintering properties, and on and on. These are, in fact, not really predictions at all since so much has been demonstrated in the laboratory already. Such developments are clearly of interest to the DoD. ARPA support of the Pratt & Whitney process for making rapidly quenched superalloy powders attests to this. It is also clear

that such developments have much broader applications than for superalloys alone, and could have a tremendous beneficial impact on the civil sector, which is all to the good.

It is not nearly so easy to look at a specific laboratory finding that an amorphous alloy has a thermoelectric coefficient 50 times that of its crystalline equivalent, and to predict that we will have a thermoelectric power station in five years. The finding does, however, almost demand that we take another look at thermoelectric properties, for we now have a new method by which we can radically alter such properties. The same is true for superconductivity, for ferromagnetic and other magnetic materials, for dielectrics, photovoltaics, piezoelectrics, magnetostrictive materials, semiconductors, and a host of other useful or curious materials and material properties.

It is really difficult to practice restraint in predicting the potential applications which might come out of such research. The fact that amorphous metals are a new class of materials, a new frontier, a new metallurgy, cannot be overemphasized. Yet amorphous materials are only one class of metastable materials. It would be possible to make every one of the predictions mentioned earlier for powder metallurgy without once considering the true amorphous state. It must be emphasized again that the processes and techniques being developed to exploit the truly amorphous state are the very ones which can and do excite one's imagination in the consideration of the powder technology.

There can be no doubt that the successful exploitation of superplasticity, of new classes of alloys, of new capabilities in instrumentation, of new capabilities in energy generation or storage, etc., would be of tremendous interest and value to DoD. Nor can there be any doubt that the civil sector would reap many benefits as well. One can therefore predict with near certainty that DoD needs will be furthered by advancing the state-of-the-art in metastable materials. The fact that commercial industry has much to gain as well is a substantial plus. The Government has the rare opportunity of being a partner with, rather than being only a customer of (or, as some might say, a competitor of) private industry in the exploitation of the enormous potential of metastable materials.

RECOMMENDATIONS FOR ARPA ACTION

There is no way, nor is there any reason, for the Government to assume the responsibility for the total development and exploitation of metastable materials. If the potential that so many of us predict for this field is actually there, then American industry will gradually recognize that fact. We are, in fact, in the early stages of this recognition, with research and development efforts of significant magnitude under way in such organizations as IBM, Allied Chemical Corporation, Bell Laboratories, and General Electric Laboratories.

The key role that Government can play, and this seems tailor-made for ARPA, is to take positive steps to encourage every segment of private industry to recognize the potential inherent in metastable materials, and to "do their own thing". At the same time, assuredly, various parts of the DoD would continue to support research and development aimed at their own specific needs.

ARPA's role then contains three critical elements. These are:

- (1) Making information on metastable materials readily available
- (2) Identifying and encouraging key developments
- (3) Removing or abating unnecessary road blocks.

Information

The first of these tasks is relatively easy. It could be accomplished by the establishment of an information center, or by assigning to an existing information center, the task of the assembly and distribution of the world literature on metastable materials.

In the present study, more than 1000 publications relative to the field were identified. Because of the limited time available for the literature search, this sample is known to be incomplete. It is doubtful that the sample represents much more than half of the available references. Part of the difficulty lies in the tremendous diversity of the subjects and journals involved, and in the lack of universally accepted key words for filing and cross-indexing. Figure 7

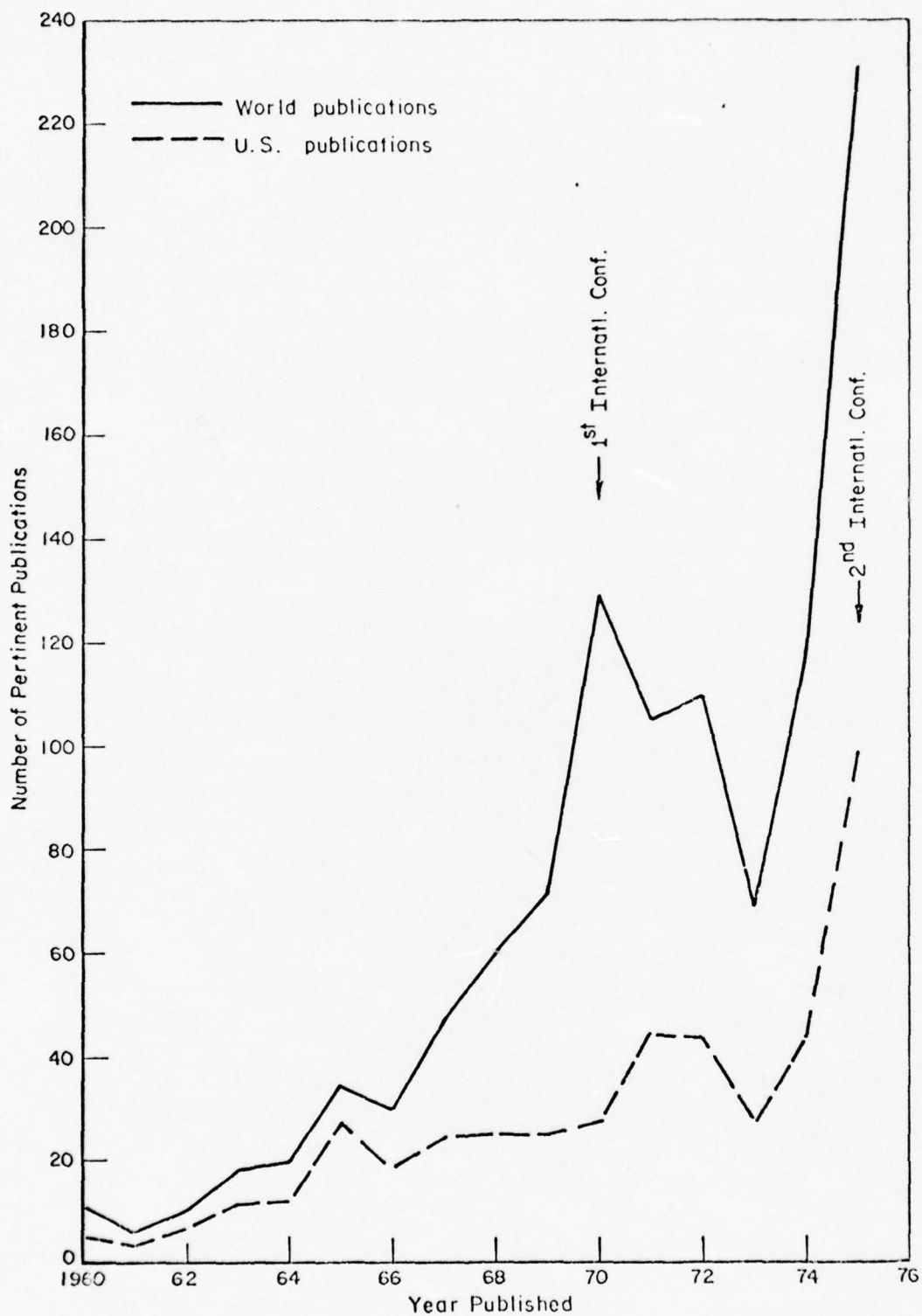


FIGURE 7. RATE OF PUBLICATION OF METASTABLE MATERIALS

illustrates the rapid increase in publications, especially foreign publications, in the last few years. If the data are representative, about half of all that has been published has appeared in the last three years. Much of this information is in a foreign language (Russian, Japanese, French, etc.) and in journals not available outside of major libraries. As a result, many researchers spend a great deal of time finding information, missing much of it, depending upon reviews which often appear several years later to catch up on foreign developments.

This situation could be greatly alleviated if an information center could provide (probably for a price) a cross-indexed abstracted bibliography of past research, an annual abstracted bibliography, a monthly or quarterly report on recent developments, and translations of selected foreign publications.

Key Developments

This is a more difficult task because it is judgmental in character. The goal is to recognize specific research problems which, if solved, could contribute to a broad advance in the technology of metastable materials. For example, one area could be in the manufacturing technology for rapidly quenched metals. A number of methods were outlined previously. Many more probably exist, and many variants and improvements to the existing technology can be anticipated. If the assessment of the potential of metastable materials is correct, the need for the most efficient manufacturing technology to produce commercial quantities of high-quality material will not be long in coming. This may be of particular importance with respect to amorphous sheet, the development of which is probably critical to most of the anticipated ferromagnetic applications. A second example might be to attempt to understand the phenomena of nucleation and growth, as well as of supercooling, in rapidly quenched materials. A better understanding of these phenomena seems sure to advance the state-of-the-art of metastable materials across the board. Such proposals should be solicited.

Judgment of key developments will have to be made by experts in the field. It is therefore suggested that ARPA establish an advisory panel with responsibilities directed specifically toward metastable materials. It is

suggested that the Metastable Materials Advisory Panel (MMAP) consist of selected members of the research community with a long-term commitment to the field and a record of accomplishment, representatives from industries which are committed to the development of the field, and representatives of various Government agencies with a commitment to the field.

Specific recommendations for members of the research community are:

- Prof. Pol Duwez, California Institute of Technology
- Prof. Nicholas Grant, Massachusetts Institute of Technology
- Prof. Bill Giessen, Northeastern University
- Prof. David Turnbull, Harvard University.

Specific recommendations for committed industries are:

- Allied Chemical Corporation
- IBM
- Bell Laboratories
- General Electric Laboratories
- United Technologies, Inc.

Specific recommendations for committed Government agencies (other than ARPA) are:

- ONR
- ERDA
- Materials Laboratory, WPAFB.

The MMAP should probably be organized by one of the university people named above, under contract, so that his organizational duties would be funded. It would also be appropriate to offer a per diem or a stipend to non-Government MMAP members. It would be the responsibility of the chairman to select the appropriate members of MMAP, to organize and schedule meetings, and to edit and report the findings of the panel.

The primary function of MMAP would be to advise ARPA on topics relative to metastable materials. These topics could include:

- (1) The need for and the character of some central information source as suggested above

- (2) Identification of key areas in which Government agencies should solicit proposals
- (3) Assessment of technical feasibility of selected research proposals
- (4) Early identification of developments of specific importance to DoD
- (5) Identification of and recommended approaches to alleviate specific roadblocks to the development of the potential of metastable materials.

It is important that members of MMAP not be excluded from submitting proposals. It is also important that membership in MMAP be reasonably open to new members from the academic, industrial, or Government sectors.

Roadblocks

There are certain areas of research which should be encouraged. It is not now, nor is it expected to be, difficult for industry to fund research which has a high probability of producing a profitable product. However, where markets are still a bit obscure and difficult to assess quantitatively, or when it is difficult to assess processing costs accurately, development is stifled. Both of these difficulties are part and parcel of the developing field of metastable materials. While everyone agrees that the potential is vast, no one is sure where the first commercial breakthrough will occur. This situation is a real and serious roadblock. It would be of outstanding value for the DoD to identify new processes and products at an early stage, fund or partially fund (perhaps sharing costs) programs to take these processes or products to the stage where they fall within the limits governing commercial risk-taking. This could involve developments taking place entirely within a commercial organization (such as the Pratt & Whitney powder program), or by a partnership between a university or a private laboratory and a commercial firm. The major stumbling block to this might very well be the Government's view on patent rights. The incentive for a private commercial organization to devote its discretionary funds to a high-risk development is perceptibly lessened by requirements that the Government obtain license-free rights to processes or products which have been developed using Government funds. This is a particularly thorny issue, involving

good, solid arguments on both sides. If a firm, mutually acceptable compromise (between the Government and industry) could be arrived at, the negotiation for development contracts as envisaged here would be greatly simplified. This would provide tremendous leverage to Government dollars as well. NASA's latest position (see Appendix C) is a good plact to start.

To be more specific, a number of patented processes (as well as some unpatented, and probably unpatentable due to their similarity to prior art) exist to make various types of powder, filament, or sheet at sufficiently high rates to produce metastable materials. In some cases, if tons of the materials made by these processes were available for sale, they would not be sold, for the market is potential, not actual. The commercial incentive is not yet great enough to attract risk-capital, but the need for the availability of these products for experimentation is great. Most laboratories are not anxious to invest their funds to develop a new process to provide other laboratories with experimental samples. Nor, in the event that they own patent rights on a process or product, are they willing to give up (hoped for) future profits in return for present Government funds to assist in speeding up the development. Unpatentable processes rarely get developed in commercial business unless they are kept very quiet (to obtain a proprietary edge). Most businesses want a patentable or a patented process to minimize the effect of possible competition, or to profit by licensing. Business will accept an unpatented or unpatentable process or product only if the risk is very low and the profit potential very clear.

This particular roadblock could be at least partially broken by DoD support of new processing techniques to the point where reasonable quantities of materials could be provided to other investigators at other laboratories. It is now possible to purchase sample quantities of some amorphous metals from Allied Chemical Corp. in the form of ribbons or filaments. Virtually all of the material being used for research on other than the Allied products is made by the investigator himself on his own apparatus. This greatly increases the cost of the product to the investigator, and frequently has little value to him in terms of the properties in which he is interested. The nuclear physicist interested in radiation effects on an amorphous alloy (other than the several commercially available) is faced with a long lead time in learning the lore of rapid quenching before he can perform his first experiment.

It would serve a very useful purpose if DoD nucleated a program either in-house in a Government laboratory, or in university or private laboratories, to not only develop some of the promising processes, but to provide experimental quantities of materials at nominal or no cost to other qualified investigators. The leverage provided by this mechanism has been amply verified in the past. Consider, for example, the tremendous amount of work using Allied's materials. For many investigators there are no other materials available.

This kind of support is almost vital to the development of a fundamental understanding of the phenomena observed in metastable alloys. Fundamental studies, other than the purely theoretical, require sample materials. Further, a fundamental understanding of the phenomena observed is almost vital to the commercial exploitation or to the invention, development, and technical application of new products and devices.

The whole area of roadblocks should be reviewed by MMAP with the aim of formulating specific suggestions for their alleviation.

CONCLUSION

It is the unqualified judgment of many scientists of international stature that the field of metastable materials is one of the most promising and one of the most challenging ever to confront the materials scientist. If the assessment is correct, the anticipated developments will have profound and beneficial effects on both DoD and civilian industry. The objective of accelerating the exploitation of the field by encouraging information exchange, by identifying and supporting research in key areas, and by diminishing the effects of roadblocks, is one which ARPA could accept and accomplish by encouraging and coordinating the efforts of the academic, industrial, and Government sectors.

As a first step in encouraging information exchange, it is recommended that this report be distributed to each of the individuals listed in Appendix A, with a request for a critical review of its contents.

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APPENDIX A

NAMES AND AFFILIATIONS OF RESEARCHERS CONTACTED

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APPENDIX B

REVIEWS AND COMMENTARIES FOR FURTHER READING

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REVIEWS AND COMMENTARIES FOR FURTHER READING

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APPENDIX C

NASA POLICY ON PATENTS AND INVENTIONS

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Funding Options and Corresponding Invention and Data Rights Policy

It is NASA policy:

- to acquire rights in inventions and data developed in the performance of NASA funded experiments;
- to insure the widest dissemination of the results derived from space investigations through publication in scientific and technical journals or other appropriate media; and
- to utilize its rights in inventions, patents, and data in a manner to provide incentives for commercialization of space technology.

In furtherance of these policies, NASA's position as to rights to inventions and data developed in this project will be governed by the user's plans and intentions to commercialize the results of the experiments and the degree of private funding involved as set forth below.

1. Privately Funded (U.S. only)

When the user furnishes the experiment (without charge to the Government) and reimburses the Government for his pro rata launch costs, NASA will not acquire rights to the user's inventions, patents, or proprietary data utilized or developed in performance of the experiment. However, the user will be required to furnish NASA with a general description of the proposed investigation and its objectives in the technical proposal.

Following the flight, the Principal Investigator will be required to submit a report describing in general terms the experiment results and reports indicating the progress towards commercialization of the results. It is not intended to require the inclusion of proprietary data in the above reports.

2. Cost Sharing (U.S. only)

NASA is prepared to consider favorably the negotiation of an arrangement whereby the cost sharing user will be granted a conditional exclusive position in inventions and data developed during the investigation. The extent to which rights may be granted will be governed by the proposed degree of private funding and the potential commercial application of the experiment results. The grant will be conditional upon the user's

compliance with the proposed cost sharing plan and his efforts toward commercialization of the results. Those proposing on a cost sharing basis and desirous of an exclusive arrangement should include in their proposal a plan for commercialization of the results of the experiment and the extent of invention and data rights sought.

3. NASA Funded

NASA is required by law to take title to inventions made in developing and carrying out a NASA funded experiment; however, the Agency will give favorable consideration toward waiving title to such inventions to the proposer in the event he submits a plan which in NASA's view gives promise of commercializing the results of the experiment.