RAW MATERIALS, MELTING, RECYCLING AND PRIMARY PROCESSING

CRITICAL REVIEW: RAW MATERIALS, MELTING, RECYCLING AND PRIMARY PROCESSING

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Abstract

This paper will review some of the developments in the areas of sponge production, melting, recycling and primary processing since the last conference four years ago. As many of the developments in this general area are proprietary, it is difficult to present an all-encompassing viewpoint. Nonetheless, there are still many areas which can be discussed in an open format, and as many of these as possible will be addressed.

Introduction

Examining the world titanium industry over the past four years and comparing it to the prior twenty-five to thirty years, one readily concludes that the past few years have seen more change in the industry than any comparable period. For example:

a) The political developments in Russia have brought the world's largest capacity producer much closer to the world market than ever before. The need for hard currency in this region of the world will undoubtedly bring a substantial amount of sponge and/or mill product to the market at very competitive prices.

b) The economic recession in the Western World has taken a heavy toll on the titanium industry. For example, in 1991 U.S. shipments suffered the largest percentage drop from the prior year (34.2%) in over 30 years. (See Table I).

c) RMI Titanium Co. closed its 24 M-lb/yr sponge facility in early 1992 after over 35 years of operation. This reduces the U.S. sponge capacity from 67 M-lbs/yr in 1991 to 46 M-lbs/yr, a 31.3% decline.

d) TIMET announced an agreement to join Union Titanium Sponge Corporation (UTSC, a Japanese consortium) in the construction of a 22 M-lbs/yr vacuum distillation facility at TIMET's Henderson, NV sponge plant. This facility, which will be operational in early 1993, will be the only U.S. vacuum distillation facility. TIMET plans to idle a comparable amount of its current leached sponge

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capacity when the distilled sponge production begins.

e) After 40 years of almost exclusively relying on vacuum arc melting, cold hearth melting, either plasma or electron beam, has emerged as a viable production melt practice. This new melt practice is already qualified for premium rotating grade applications in gas turbine applications.

These changes are certainly dramatic in an industry which usually undergoes evolutionary rather than revolutionary changes. Coupled with other related developments, it is easy to argue that the face of the worldwide titanium industry will continue to change far more rapidly than past history would suggest.

TABLE I. - U.S. Industry Mill Product Shipments by Year and Sorted by Percentage Change from Prior Year

Year	Shipments (M-Lbs)	1 Year Change	Year	Shipments (M-Lbs)	1 Year Change
1951	0.2		1958	3.3	- 60.7%
1952	0.5	150.0%	1991	34.2	- 34.2%
1953	2.2	340.0%	1982	36.6	- 28.2%
1954	2.6	18.2%	1971	22.5	- 22.4%
1955	3.8	46.2%	1983	31.9	- 12.8%
1956	8.1	113.2%	1968	23.8	- 12.8%
1957	8.4	3.7%	1975	31.3	- 10.3%
1958	3.3	- 60.7%	1986	41.7	- 9.7%
1959	7.8	136.4%	1970	29.0	- 9.1%
1960	9.2	17.9%	1963	10.8	- 8.5%
1961	11.4	23.9%	1976	28.8	- 8.0%
1962	11.8	3.5%	1981	51.0	- 5.9%
1963	10.8	- 8.5%	1990	52.0	- 5.6%
1964	15.4	42.6%	1967	27.3	- 2.5%
1965	18.7	21.4%	1951	0.2	-
1966	28.0	49.7%	1985	46.2	1.8%
1967	27.3	- 2.5%	1962	11.8	3.5%
1968	23.8	- 12.8%	1957	8.4	3.7%
1969	31.9	34.0%	1987	44.6	7.0%
1970	29.0	- 9.1%	1977	30.9	7.3%
1971	22.5	- 22.4%	1989	55.1	10.9%
1972	25.3	12.4%	1979	46.2	11.1%
1973	29.0	14.6%	1988	49.7	11.4%
1974	34.9	20.3%	1972	25.3	12.4%
1975	31.3	- 10.3%	1973	29.0	14.6%
1976	28.8	- 8.0%	1980	54.2	17.3%
1977	30.9	7.3%	1960	9.2	17.9%
1978	41.6	34.6%	1954	2.6	18.2%
1979	46.2	11.1%	1974	34.9	20.3%
1980	54.2	17.3%	1965	18.7	21.4%
1981	51.0	- 5.9%	1961	11.4	23.9%
1982	36.6	- 28.2%	1969	31.9	34.0%
1983	31.9	- 12.8%	1978	41.6	34.6%
1984	45.4	42.3%	1984	45.4	42.3%
1985	46.2	1.8%	1964	15.4	42.6%
1986	41.7	- 9.7%	1955	3.8	46.2%
1987	44.6	7.0%	1966	28.0	49.7%
1988	49.7	11.4%	1956	8.1	113.2%
1989	55.1	10.9%	1959	7.8	136.4%
1990	52.0	- 5.6%	1952	0.5	150.0%
1991	34.2	- 34.2%	1953	2.2	340.0%

Source: U.S. Bureau of Mines

Raw Materials

Production/Capacity Statistics. Table II provides a summary of world sponge capacity from 1981-1991. Overall, world-wide capacity changed very little over that span, ranging from 227 M-lbs in 1981 to 263 M-lbs in 1984 and 1990 - a modest 15% change over the entire period. However, the pie-chart in Figure 1a shows the 1990 breakdown by country, with Figure 1b showing the projected breakdown for 1992. As noted earlier, Russia has the largest capacity, with Japan ranked second and the U.S. third, even further behind Japan with the closing of the RMI sponge plant. Given the current economic environment in the titanium industry, it is difficult to project much of any substantial increase in capacity over the short term. The only

TABLE II. - World Sponge Capacity(1)

Capacity (m-lbs)	'81	'82	'83	'84	'85	'86	'87	'88	'89	'90	'91
U.S.	61.0	67.0	67.0	67.0	65.0	61.0	56.0	58.0	64.0	67.0	67.0
Japan	60.0	71.0	75.0	75.0	69.0	69.0	51.0	51.0	59.5	63.5	63.5
Europe	8.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0
Subtotal	129.0	149.0	153.0	153.0	145.0	141.0	118.0	120.0	134.5	141.5	141.5
Russia (C.I.S.)	92.0	100.0	100.0	104.0	106.0	106.0	110.0	110.0	115.0	115.0	115.0
China	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Total	227.0	255.0	259.0	263.0	257.0	253.0	234.0	236.0	255.5	262.5	262.5

Sources:(1) Titanium Statistical Review: 1981-1990 Published by U.S. Titanium Development Association (1991 Values Estimated).

added capacity known by the author to be under construction at this time (other than the TIMET distillation facility) is the 24-cell, roughly 7 M-lb capacity, electrolytic plant being constructed in Terni, Italy by Ginatta Torino Titanium. It should be noted, however, that RMI discontinued its operation of a single Ginatta pilot cell in 1991.

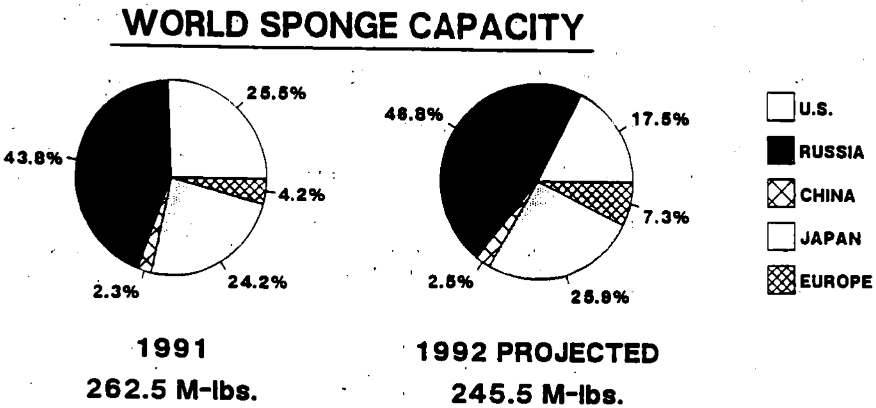

Figure 1a and 1b - Percentage Breakdown of World Sponge Capacity.

Tables III and IV list the sponge production statistics as a percentage of overall capacity for the U.S. and Japan respectively. This data shows the historical "boom-bust" cycle that has plagued the titanium industry for so long (See also Table I). In the U.S., sponge production as a function of capacity ranged from 41.6% to 86.9% while Japanese capacity utilization ranged from 31.1% to 91.2%.

Since the aerospace industry (military plus commercial) typically accounts for well over half of titanium consumption, it is generally felt that expansion into non-aerospace (industrial) markets will lessen the cyclical

TABLE III. - U.S. Production Statistics(1)

	'81	'82	'83	'84	'85	'86	'87	'88	'89	'90	'91(2)
Sponge Production (m-lbs)	-	-	27.9	48.7	46.5	34.8	39.4	49.1	55.6	54.4	29.5
% of Capacity	-	-	41.6	72.7	71.5	57.0	70.4	84.6	86.9	81.2	44.0
Ingot Production (m-lbs)	92.4	53.1	52.9	80.0	70.8	70.2	74.4	85.7	91.0	81.1	54.9
% of Capacity	92.5	45.2	43.7	57.1	50.6	50.1	50.6	58.3	61.9	54.2	37.1
Scrap Consumed (m-lbs)	29.6	17.0	20.3	31.1	29.4	33.0	36.1	39.8	38.8	33.0	25.1
% of Ingot Production	32.0	32.0	38.4	38.9	37.3	47.0	48.5	46.4	42.6	40.7	45.7

TABLE IV. - Japanese Production Statistics(1)

	'81	'82	'83	'84	'85	'86	'87	'88	'89	'90	'91
Sponge Production	54.7	37.1	23.3	33.9	49.1	32.1	22.2	36.1	47.0	56.5	-
% of Capacity	91.2	52.2	31.1	45.2	71.2	46.5	43.5	70.7	79.0	89.0	-

Sources: (1)Titanium Statistical Review: 1981-1990 Published by U.S. Titanium Development Association and (2)1991 Mineral Industry Surveys, U.S. Bureau of Mines, February 28, 1992.

nature of the industry. Much effort is being expended to develop such markets. For example, the automotive market is considered a strong candidate for a new industrial market for titanium.[1-5] Since cost is overwhelmingly the key driver in this market, special low cost titanium alloys have been developed for this market. Daido[6] has developed a free-machining alloy grade to help reduce the high machining costs in connecting rod manufacture. TIMET has developed[7] a low cost substitute for Ti-6Al-4V for use in exhaust valves and/or connecting rods. Such efforts hopefully will not only lead to applications in the automotive arena but also in other non-aerospace applications as well.

Ultra-High Purity Titanium. Although it is very small compared to the conventional markets for titanium sponge, there is a steadily increasing market for ultra-high purity titanium for use on integrated circuits for the electronics industry. Within this market segment, purity levels are often referred to as 4-9's (99.99%), 4-9's, 7 (99.997), 5-9's (99.999%) etc... but only metallics are considered in this figure. For example, a 4-9's product has less than 100 ppm (total) of all tramp metallics (Fe, Ni, Cr, Al, V, Mn...) but could contain several hundred ppm of interstitials such as oxygen, nitrogen, etc. Currently, the market for this product is moving from about 99.993 (4-9's, 3) towards a 5-9's product. While the U.S. market is only roughly in the 15,000 to 20,000 lbs/yr range, the ultra-high purity product commands a significantly higher price than conventional sponge.

The high purity product is most often produced by a molten salt electrorefining similar to the process cited by the U.S. Bureau of Mines.[8,9] Special attention is paid to all processing steps thru melting in order to reduce tramp contamination. Some recent patents[10,11] relating to improved production methods have been issued during the last few years.

Melting

Cold Hearth Melting: Arguably the most dramatic progress in the melting arena over the last several years has been the emergence of the cold hearth melting process as a production tool. There are two types of cold hearth furnaces currently being used - those which use electron beam guns for melting (EB) and those which use plasma torches (Plasma). Table V lists some of the pro's and con's of each type of furnace. Perhaps the most significant drawback to the EB furnace is the evaporative loss of high vapor pressure elements such as aluminum and chromium. On the other hand, the plasma process has limited hydrogen removal capability and a more turbulent pool. Also shown in this table is the poorer melting power efficiency of these processes compared to VAR, establishing these processes as higher cost melting practices. However, both processes appear to be very effective in their primary function - removing potential defects.

TABLE V. - Comparison of Melting Systems

	E.B. Cold Hearth	Plasma Cold Hearth	VAR
Evaporative Loss	Yes	No	No
Hydrogen Removal	Yes	Limited	Yes
Power Consumption (KWH/kg)	2.4	3.0	1.0
Loose Feed Capability	Yes	Yes	Limited
Sponge Feed Capability	Limited	100%	100%
Furnace Cost/Lb Capacity	Highest	High	Moderate
Maintenance Cost	High	High	Moderate
HDI Removal	Yes	Yes	No
LDI Removal	Very Good	Very Good	Limited

Although several production "in-spec" heats of Ti-6Al-4V were produced by 1988,[12] it was the tragic United 232 incident at Sioux City in July of 1989 that significantly accelerated efforts to employ this process on a production basis. The initiation site for the crack which ultimately led to the fan disc failure in the United 232 incident was found to be associated with an undissolved burnt sponge particle, otherwise known as a Type I low density inclusion (LDI). Such burned sponge particles, when high enough in nitrogen content, do not melt during the melting process and hence must be dissolved by the molten pool. For a given particle size, there is a critical residence time in the molten pool (at a given temperature) which must be exceeded before the particle will be dissolved. The advantage, and hence utility, of the cold hearth melting process is that the time material spends in the hearth - known as residence time - is independent of power supplied to the hearth. Thus, as opposed to VAR melting, residence time in the molten pool is theoretically infinitely variable. It is felt that the cold hearth process should be capable of dissolving or trapping "all" potential LDI formers. In addition, the hearth has been shown to be essentially 100% effective[13,14] in trapping other high melting, high density defects (such as tungsten particles) known as HDI's (high density inclusions). Because of the well established benefits of this process in terms of "eliminating" LDI's and HDI's some engine producers are now specifying hearth melted material for critical component manufacture.

As would be expected with such a relatively new process, there are still some unanswered questions regarding cold hearth melting:

a) Does hearth melting remove 100% of LDI's and, if so, can designers actually take advantage of this? This leads to a related issue about NDI and the ability to verify a "defect free" condition.

b) Is there a difference between plasma vs. EB melted quality?

c) Is it necessary to VAR after hearth melting? Today, all hearth melted material is subsequently VAR processed.

d) What about the economics of hearth melting in general (hearth vs. VAR) and EB vs plasma?

Since most rotating gas turbine engine components are designed on the basis of low cycle fatigue and operate at very high stresses (hence have relatively small critical flaw sizes), the clean ingot technology could have a major impact on the design/service life of such components. However, airframe structures which generally operate at lower stresses and are designed for crack growth (ie. damage tolerance) are less likely to be affected by such technology. As a result, the large engine producers (principally GE) have spearheaded the efforts to bring this process to a full production status. They have incorporated this melting process into their specifications and continue to work on improvements and a better understanding of the process.

An example of the on-going efforts is the current A.F. sponsored program[14] being conducted by G.E. to "establish the hearth melt 'only' processes and procedures for preparation of premium quality alloys for gas turbine engine components". Today all hearth melted material is given a final VAR step. The A.F./G.E. program is evaluating elimination of the final VAR melt step.

One of the principle techniques to be used in the A.F./G.E. program will be to seed the ingots with a high number of artificial seeds (nitrided sponge particles) and subsequently ultrasonically inspect (UI) the product as billet and bar. It should be noted that the product can only be pronounced as 'clean' as the UI capability. From a conservative design standpoint, one could only assume a defect size equivalent to (or slightly below) that to which the material can be inspected. This has brought to bear a considerable amount of effort into improved UI capability.

It is also important to note that cold hearth melting is being applied to non-aerospace or non-premium grade product. In such cases, hearth melting is strictly driven by economics wherein low cost forms of scrap are recycled thru the hearth, typically at a much faster melt rate than premium grade product. In these instances, up to 100% scrap (such as turnings) can be recycled.

<u>Fine Sponge</u>. At the 1988 International Conference, J. Hall[15] reported on a U.S. Patent[16] which disclosed the method of rendering sponge particles "finer" than normal in order to facilitate the dissolution of undesirable LDI formers. There are two key variables in determining the time required for dissolution of a particle:

a) Particle size

b) Dissolution rate (dependent on molten pool temperature, chemistry, stirring...)

The fine sponge process takes advantage of a smaller particle size to promote particle dissolution. By shearing and screening processes, the largest sponge particle, and hence potential LDI former, can be substantially reduced. TIMET implemented the fine sponge process for VAR in 1988 by reducing the maximum sponge particle size from about 8mm dia. to 3.4mm dia. This change in particle size has contributed to roughly an 8-fold reduction in LDI incidence rate. Such an improvement was demonstrated over a production run of over 5 million pounds of product.

A logical extension of this development could be the combining of the cold hearth melting process with the fine sponge approach. The benefit might not only be greater assurance of LDI dissolution but also economic savings. The finer particles will require less residence time and hence a faster melt rate could be used. Using the relationships cited by Hall[15], wherein the time to dissolve a cylindrical particle is proportional to the square of its radius, halving of the particle size reduces the dissolution time by a factor of four.

Computer Modelling of VAR and Hearth Melting. The vacuum arc remelting processes is very complex. There are many variables which can affect ingot quality from the standpoint of homogeneity, and soundness. Such variables can also affect product yield thru their impact on grain structure and surface quality. It is usually difficult and very expensive to adequately quantify the effects of the numerous melting variables such as voltage, current, stirring, etc... In order to more efficiently evaluate these effects, computer modelling of the VAR process has been developed. Such a model is discussed by J. R. Faber[17] in a recent publication. Faber begins by showing the correlation of the model vs. prior published data in predicting molten pool depths as a function of melt rate (power). He then shows the excellent correlation between actual thermal measurements on an instrumented crucible wall during a production VAR melt vs. the model predictions. Having established the validity of the model, he then goes on to show how the model can be used to predict segregation tendency in a difficult to melt alloy (Ti-10V-2Fe-3Al) by combining the Tiller Equation[18] with the model's predicted temperature gradients and solidification rates. By the Tiller Equation, it is shown that dendritic freezing and microsegregation are avoided when:

$$\frac{GD_L}{V} \geq \text{ie, } -MC\left(\frac{1-k}{k}\right)$$

where G = thermal gradient at the liquid interface; D_L = diffusivity of the solute (Fe in the case of Ti-10V-2Fe-3Al) in the liquid; V = freezing velocity of the interface. These values on the left-hand side of the equation are melting variables (D_L is affected by stirring). The variables on the right-hand side are a function of the solute element of interest: M = slope of the liquidus at the melting point; C = solute content in the liquid away from the interface and k = partitioning coefficient (ratio of solidus content vs. liquidus content). By rearranging the terms,

$$\text{Tiller Factor} = \frac{GD_L\, k}{VMC(1-k)} < 1 \; ,$$

Faber uses the Tiller factor to determine if segregation can be avoided (ie. segregation is avoided if the Tiller factor is less than one).

Since the melting variables can be calculated by the model, and the material variables can be approximated from binary phase diagrams, one can use the model to predict the impact of melting variables on segregation tendency and thereby design a suitable melt practice which avoids the segregation.

Such modelling can be used to solve a variety of melting problems. For example, post-melt thermal gradients can be altered by melt practice in such a way so as to minimize or eliminate cracking of brittle ingots such as alpha-two or gamma titanium aluminides. Also, the modelling process can be used to predict residence time/temperature profiles for dissolution of burned sponge particles which can lead to low density inclusions (LDI's).

The modelling technique can also be used to study hearth melting as well. It is clearly a very powerful and useful tool which will continue to evolve as demands on melting quality become more stringent.

Scrap Recycle

DOSS Process. RMI Titanium Co. (J. L. Fisher) discloses a "process for deoxidizing refractory metals such as titanium which contain less than about one percent oxygen" in two recent patents[19,20]. The process is referred to as the DOSS (De-Oxidation in the Solid State) process. It is intended to be used on section sizes less than about 4.7mm (.185") in thickness, typically for powder, chips, turnings, sheet or foil. The process consists essentially of the following steps:

a) Placing the "high" oxygen material (typically .2 to .3% oxygen) in a container with about one tenth by weight as much deoxidizer plus carrier. The preferred deoxidizer is calcium and the preferred carrier is sodium. The calcium to sodium ratio is about 1:4 to 1:10.

b) Heating the combined substances to roughly 900°C to 1000°C under vacuum or inert gas for 2 to 12 hrs.

c) Distilling off the carrier (optional)

d) After cooling the product to room temperature, crushing if necessary then acid leaching, rinsing and drying.

The patents cite examples wherein samples originally containing .2 to .3% oxygen are reduced to about .025 to .055% levels. Thus, oxygen is commonly lowered by roughly 65% to slightly over 90% in some cases.

A similar process for oxygen removal from "bulk" titanium is also shown by Okabe etal[21] in which they employed calcium plus $CaCl_2$ flux. They reported reductions in oxygen from 800 to 1200 ppm down to less than 100 ppm (30 to 90 ppm) by exposing small cross-section titanium samples to the Ca + $CaCl_2$ mixture in the temperature range of 900°C to 1000°C for 24 to 60 hrs. This process is essentially that cited by Rostron[22] in 1958. In that case, Rostron was using the calcium deoxidation as a second reduction step following a primary step which was incapable of removing enough oxygen. The utility of these deoxidation processes is, as usual, driven by economics. If the cost of titanium scrap (eg. turnings) plus the cost of deoxidation is less than that of virgin materials (sponge + master alloy), then the process can be viable. This assumes, of course, that the deoxidized material can be melted and processed on an equivalent cost basis as the virgin material.

Primary Processing

Processing Windows. One of the key's to producing a high quality mill product such as aerospace quality billet or bar is the ability to produce a fine uniform macrostructure as early in the conversion process as possible. Since an as-cast ingot contains not only very coarse grains but also a wide range of grain sizes and morphologies, it is usually a primary objective of the early ingot conversion steps to induce recrystallization in order to refine the grain size and produce a uniform grain size. Failure to do so properly can result in unacceptable product containing undesirable defects such as strain induced porosity (S.I.P.), continuous grain boundary alpha, blocky alpha, etc..

In order to provide for complete and uniform recrystallization, processing windows[23] such as that shown schematically in Figure 2 are being used. While it is readily apparent in this figure that work conducted below the beta transus is very effective in driving complete recrystallization, one does not always have that option available. For example, metastable beta alloys and beta rich alpha-beta alloys have such low beta transus values and high flow stresses at the subtransus temperatures, it is often impossible to effectively use subtransus work to drive recrystallization. Even in alloys with higher beta transus values, section size requirements often preclude the use of subtransus work. In such cases, work above the beta transus temperature must be used to drive recrystallization.

The schematic in Figure 1 shows that, for a given amount of work, there is an optimum combination of work temperature and anneal temperature in order to provide complete recrystallization. Usually, it is desirable to drive recrystallization at as low a temperature as possible in order to keep grain size as fine as possible.

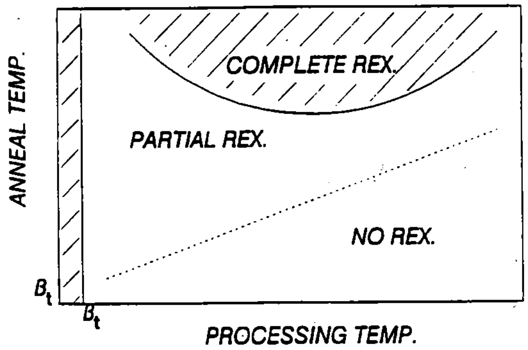

Figure 2 - Schematic representation of a Processing Window for a given amount of applied strain (work).

This philosophy of properly controlling thermomechanical processing (TMP) variables to control recrystallization is not limited to ingot conversion practices. A recent patent by Bhowal[24] etal. discloses a similar concept used in the production of fine grained titanium forgings. By this method, isothermally beta forged components are held in the isothermal dies for a sufficient time to allow recrystallization to occur.

The Next Four Years..

Driven by product quality and/or production cost demands, and with work currently directed in these areas, it seems rather straightforward to predict some of the areas where significant progress will be made over the next four years:

a) Low Cost Sponge Production. It has long been a goal within the industry to reduce production costs by employing a continuous sponge making process instead of the current batch processes. Recent patents[25-27] in this area suggest that substantial progress will be made over the next few years, although implementation of a production facility would appear to be several years away.

b) Improved Ultrasonic Inspection. With the improved quality derived from efforts such as cold hearth melting and "fine sponge", there is now tremendous pressure on the non-destructive inspection community to improve overall capability. It is difficult from a design standpoint to take advantage of "clean" material unless there is a method of verifying its quality. We can expect not only improvements in the inspection instrumentation itself, but also enhancements in the materials inspectability thru controlled thermomechanical processing.

c) Cold hearth melting will see a significant advancement in the development and implementation of sensors specifically designed for the process. Sensors which can measure molten pool temperature and depth (volume) will be used to verify residence time in the hearth. Also, particularly for the E.B. systems, real time analytical sensors will determine pool chemistries in order to be able to adjust alloy content to accommodate evaporative losses.

d) Metal Matrix Composites. With the extensive research now on-going relative to metal-matrix composites, especially very high temperature composites, novel methods are emerging[28,29] for production of low cost foils as well as low cost methods of coating fibers directly. The viability of many advanced engines and airframe structures seems to be intimately linked to development of these advanced composites.

All things considered, the next four years appear to be shaping up as a period of adjustment to the recent changes, highlighted by progress resulting from the changes.

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