A Metallurgical Evaluation of a New Tungsten Product

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An experimental program was conducted to evaluate a new form of granule tungsten produced via the hydrogen reduction of tungsten hexafluoride. The as-produced granule tungsten is characterized by both an unusually high purity and a very fine grain size. These characteristics can be retained in massive forms of the metal by consolidation of the granules with a gas-pressure bonding process. Consolidation by this method also offers close control over both dimensional tolerances and the degree of densification. Sheet bars thus prepared were rolled to sheet using practices commensurate with those being applied to current commercial materials. Sheet evaluation studies in comparison with commercial tungsten sheet included softening and recrystallization behavior, bend transition temperature, and intermediate- to high-temperature tensile properties. The granule sheet showed superior resistance to recrystallization and lower transition temperatures; it also showed improved tensile strength, especially after high-temperature thermal cycling.

Introduction

Because of its high melting point, tungsten is of considerable interest as a structural metal in those aerospace applications where high-temperature environments are encountered. This property alone has justified the efforts of the metalworking industry to cope with its major disadvantages, which include difficulty in consolidation and fabrication as well as poor low-temperature ductility.

A considerable research and development effort has been under way for some time to overcome and/or bypass the aforementioned problem areas. These include basic studies concerned with achieving a better understanding of the reasons for the lack of low-temperature ductility,[1, 2] alloy development programs,[3, 4] and applied studies aimed at the development of improved processing techniques.[5]

One of the important findings from the basic research is that impurity elements, including metallics as well as interstitials,[1, 6] contribute to the low-temperature brittleness of tungsten. It has also been recognized that grain size and shape play important roles in the workability as well as low-temperature ductility. Thus, optimum workability and ductility is currently achieved in wrought tungsten products processed via the powder metallurgical route by methods that yield a fine, elongated grain structure. A significant purity advantage over powder metallurgy tungsten can be achieved by vacuum arc melting or by electron-beam melting. Unfortunately, however, these melted products are characterized by an extremely large grain size that renders hot working of these difficult and expensive. Recently, the combination of high purity and fine grain size has become available in a new granular grade of tungsten. This article summarizes some of the unusual metallurgical characteristics observed for this material, both in its as-produced form and after consolidation and fabrication to a sheet product.

Characterization of the Product

Granular tungsten is produced via the reduction of tungsten hexafluoride with hydrogen. The product consists of individual tungsten spheres with a size range of 200 to 600 μ and a typical average diameter of about 475 μ. Table 1 compares representative chemical analyses of the granules with those of various tungsten products prepared from commercial tungsten powders. As shown, the granules have a significantly lower impurity content than commercial tungsten powder products even after purification of the latter by electron-beam and vacuum-arc melting.

As shown in Fig. 1, the structure of individual granules consists of very fine, columnar grains radially oriented about a central core. Measurements from electron micrographs show that the widths of the individual grains generally fall in the range of 0.5 to 1 μ. Because of the small grain size and the presence of some internal lattice strain, the average hardness of the as-produced granules is quite high, i.e., around 1000 KHN.

Heating the granules at temperatures above about 3275°F results in some softening as well as some coarsening of grain structure. Hence, to retain the fine-grain size advantage of the as-produced granules in a finished product, it is desirable to

Table 1 Representative analyses of various grades of tungsten and tungsten products

	Impurity content, ppm			
Impurity element	Powder metallurgy sheet[a]	Electron-beam-melted ingot[b]	Arc-melted ingot[c]	Spherical granules
O	46 ± 28	60	12	7
N	57 ± 17	10	12.5	<10
C	<10–10	20	28.4	<10
H	1–4	<10	1.7	1
Al	10	<10	<10	<10
Ca	50	<10	<1	<5
Cr	10–50	<10	<10	...
Cu	...	<10	<1	<5
Fe	10–100	20	6.1	<10
Mg	...	<10	<1	<3
Mn	...	<10	<10	...
Mo	50	10	59	<20
Ni	10–50	<10	<1	<10
Si	10	<10	<20	<10
Sn	...	<10	<20	<10

[a] Range of values from 12 sheets prepared by the Fansteel Metallurgical Corp. for the Bureau of Naval Weapons on Contract No. NOw-60-0621-C (April 1963).

[b] Survey Report by the Universal-Cyclops Steel Corp. to the U. S. Air Force on Contract No. AF 33(600)-41917 (January 1961).

[c] Average of values from 10 ingots prepared by the Universal-Cyclops Steel Corp. on U. S. Air Force Contract No. AF 33(600)-41917 (October 1961).

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hold the temperature in the subsequent consolidation and fabrication stages as far below 3275°F as is practical.

Consolidation

Because of their size, shape, and relatively high hardness, the as-produced granules are not amenable to consolidation using normal cold compacting techniques. Thus, the granules cannot be compacted into cohesive, massive shapes using conventional steel dies or isostatic compaction in elastic containers. Conversely, it has been shown that gas-pressure bonding[7] affords an ideal method of consolidation in that, with a one-step operation, the following can be accomplished: 1) a closely controlled degree of densification; 2) metallurgical bonding between individual granules; and 3) retention of the initially fine-grain structure.

The specific parameters used in gas-pressure bonding the tungsten granules are proprietary. However, it can be disclosed that a variety of massive shapes, in densities greater than 99% of theoretical, have been successfully prepared using combinations of pressures and temperatures not exceeding 15,000 psi and 3200°F, respectively.

Figure 2 illustrates the effect of a high densification bonding cycle on the structure of the tungsten granules. The particular structures shown are representative of sheet bars, which have been prepared in sizes to 1 × 2 × 4 in. Comparison of Figs. 1 and 2 shows that the heat treatment associated with their consolidation results in some softening of the individual granules as well as in equiaxing the grain structure. For the most part, the latter consists of small grains with diameters in the range of 1.4 to 1.8 μ as illustrated in Fig. 2b. In addition, however, rings of slightly coarser grain structure tend to develop within the granules as well as at their peripheries, as shown in Fig. 2a.

Performance in Test Rocket Nozzle

Figure 3a shows a subscale rocket nozzle consolidated directly from the tungsten granules to over 99% of theoretical density using the gas-pressure bonding technique. Because of the close dimensional control during the densification process, very little machining was required to obtain the final dimensions. Thus, the nozzle was machined at ambient temperatures using the following procedure: tool, Darwin 1366 or equivalent; depth of cut, 0.020 in. (0.040 in. off the diameter); feed, 0.015 in./rev; and surface speed, 25 ft/min. Final grinding for the outside diameter was performed at room temperature using the following procedure: wheel, Sterling KA60-K6-V2 or equivalent; speed, 1750 rpm, depth, 0.001 in./pass; and feed, 2.5 in./min.

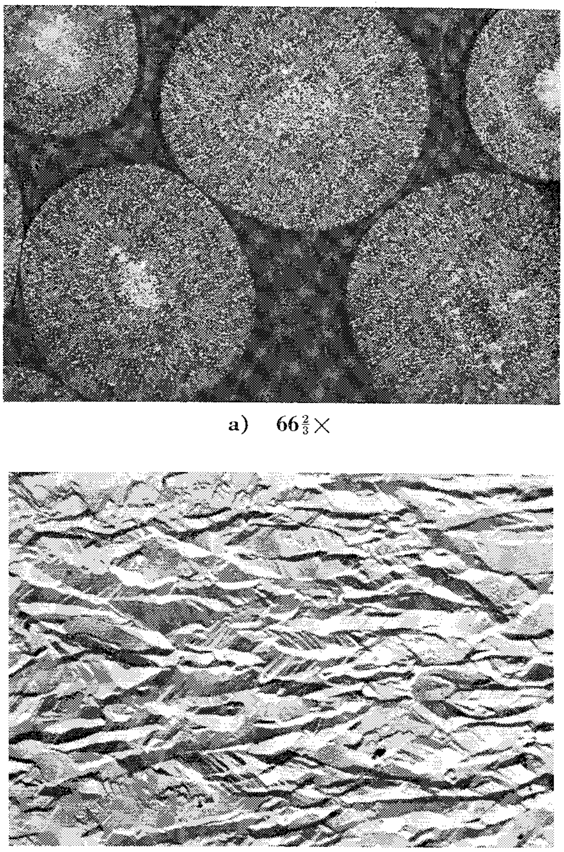
The nozzle was then fired using a double-based solid propellant generating a flame temperature of 6500°F. The appearance of the nozzle after firing is shown in Fig. 3b.

Metallographic examination after firing showed that, as a result of the severe thermal exposure, recrystallization of the tungsten granules had occurred. However, as shown by the data in Table 2, the average recrystallized grain size was quite small. In addition to retaining fine grain structure, good resistance to thermal shock was noted. Throat erosion was also minimal.

Fabrication to Sheet

Sheet bars of granule tungsten have the same advantage of direct workability as pressed and sintered tungsten bars of commercial tungsten powder. By comparison, the coarse-grained ingots obtained by normal cold-mold melting processes are amenable to rolling or forging only after using extrusion to break down and refine their initial cast structure.

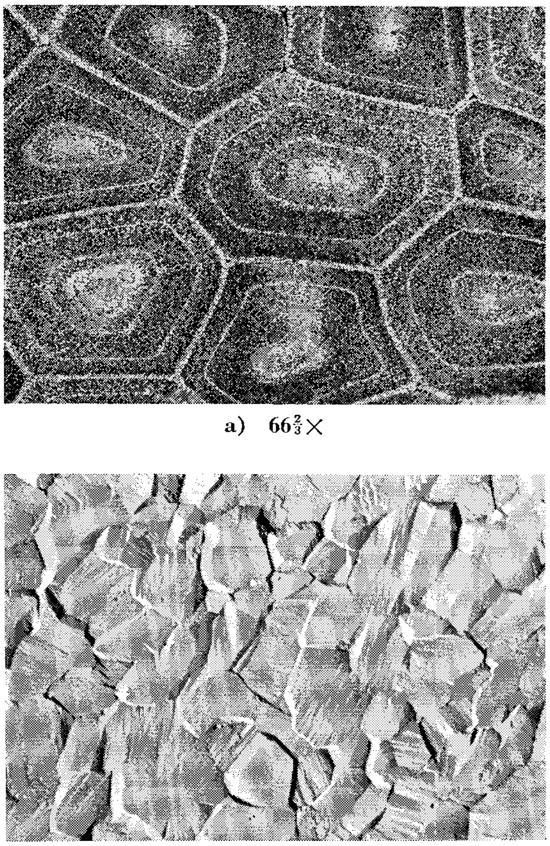
Experiences to date indicate that consolidated granule sheet-bar densities on the order of 99% of theoretical are desirable to obtain good rolling characteristics, i.e., freedom



a) 66⅔×

b) 4000×

Fig. 1 Structure of as-prepared tungsten granules.



a) 66⅔×

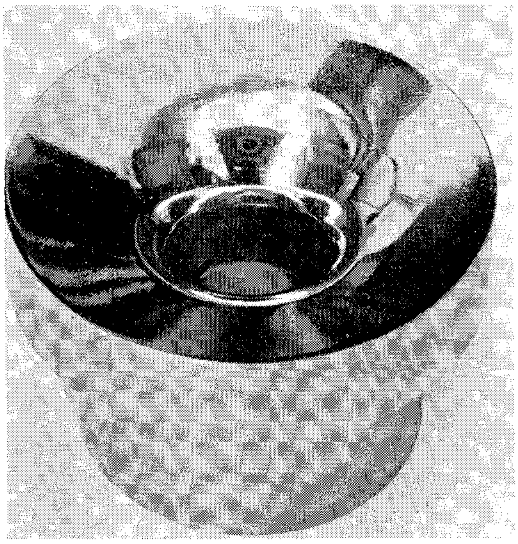
b) 4000×

Fig. 2 Structure of tungsten granules, as consolidated into sheet bar by gas-pressure bonding.

from edge and surface cracking. Such bars have been rolled directly, at temperatures from 2200° to 3270°F, through reductions totaling 95% to good quality sheet in thicknesses down to 0.040 in.

Irrespective of rolling temperature, the coarse-grain structure, introduced in localized areas in the granules during bonding, tends to be carried through to the finished sheet. However, if rolling temperatures above about 2900°F are used, additional grain growth originates from these areas. Hence, rolling at 2900°F or lower is necessary to preserve the initially fine grain structure.

Although rolling variables have not been exhaustively studied, it has been shown that essentially the same practices evolved for rolling pressed-and-sintered tungsten sheet bars can be used with equal success for rolling sheet bars of the consolidated granules. Thus, good quality tungsten sheets in sizes to 0.060 × 6 × 6 in. have been rolled using progressively decreasing temperatures over the interval of 2650° through 2200°F. The basic schedule, used to prepare much of the sheet for the property evaluations described later, is outlined as follows: 1) breakdown rolling through a 50% reduction at 2640°F; 2) intermediate rolling through a 40% reduction at 2460°F; and 3) finish rolling through a 55% reduction at 2280°F.



a) Before firing

b) After firing

Fig. 3 Solid fuel rocket nozzle (Atlantic Research Corp. design) consolidated directly from tungsten granules by gas-pressure bonding.

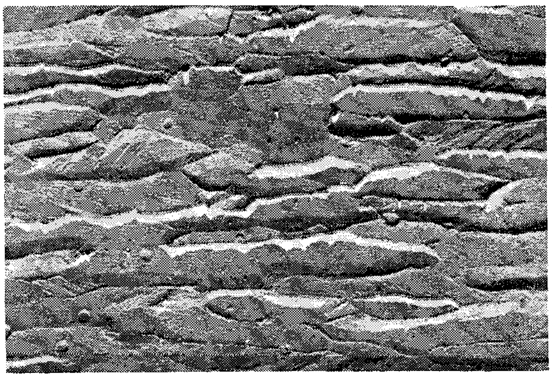


Fig. 4 Structure of 0.060-in.-thick sheet, prepared from tungsten-granule sheet bar by rolling through a 94% reduction at 2650–2280°F, 4000×.

Sheet Properties

Softening and Recrystallization Behavior

Figure 4 illustrates a structure representative of that obtained in the "granule" sheet rolled by the previously described schedule. The microphotographs at the extreme left of Fig. 5 compare this structure, at lower magnification, to that obtained in similarly processed commercial sheet prepared from tungsten powder. As is evident from these photographs, the wrought structure of the "granule" sheet consists of very fine, slightly elongated grains, whereas that of the conventional commercial sheet consists of relatively coarse and extremely elongated grains.

In the as-wrought condition, the hardness of "granule" sheet ranges from about 525 to 575 VHN, depending on initial sheet bar size and the processing schedule used. As indicated in Fig. 5, these hardnesses are somewhat above those for as-wrought conventional sheet. Annealing both types of material for 1 hr at temperatures above about 2000°F results in some softening. However, as shown in Fig. 5, the softening curves for these materials are distinctively different. The hardness of normal tungsten sheet drops very sharply on annealing over a fairly narrow temperature interval (2400°–2600°F), and thereafter decreases more slowly with increasing annealing temperatures. By comparison, the softening curve for sheet prepared from the granular tungsten decreases much more gradually with increasing temperatures through 3270°F, then more sharply at 3670°F. Upon annealing at 4170°F, the hardness drops to the same level as that achieved in conventional grades of sheet with comparable heat treatment.

As indicated in Fig. 5 and Table 3, these differences in the softening behavior of these materials result from their differences in grain growth characteristics. Thus, the abrupt drop in hardness of conventional commercial material results from the onset of recrystallization, which occurs rapidly at temperatures of 2500° to 2600°F. Further, recrystallization in this sheet results in an equiaxed grain structure of fairly uniform shape and size. In contrast, the unusual softening behavior of the "granule" tungsten sheet results from a remarkable resistance of this material to recrystallization and grain growth during high-temperature annealing. Moreover, the mechanism by which new grains are formed in

Table 2 Grain size in tungsten rocket nozzle after firing

	Grain size	
Location	Diameter, mm	ASTM
Exterior surface	0.115	3.6
Throat surface	0.053	5.8

this material is distinctly different from that observed conventional commercial sheet and bar stock. Thus, the small, elongated grains in the wrought "granule" sheet tend to retain their original shape and only coarsen slightly as annealing temperature is increased from 2550° through 3630°F. However, on annealing at 2550°F, significant grain growth is initiated in the coarse-grained areas that originated in the gas-pressure bonding operation. This growth occurs preferentially in the direction of the rolling plane and proceeds at the expense of the fine-grained areas. The extent of this preferential grain growth increases with increasing annealing temperatures but at a surprisingly low rate. Thus, even after annealing for 1 hr at 3630°F, a substantial portion of the structure remains extremely fine grained.

Bend Ductility

Both "granule" and conventional tungsten sheet show a fairly narrow temperature range within which the bend behavior changes from ductile (0–2 *T* bend values) to brittle (<16 *T* bend values). Bend values at 4*T* offer a convenient means of comparing the effects of processing parameters on the ductile-to-brittle transition temperature of both types of materials. Figure 6 summarizes the results of such a study.

As with conventional tungsten sheet, increasing the amount of "cold" reduction is beneficial in lowering the transition temperature of sheet prepared from the granules. With an equivalent amount of cold work, sheet prepared from the granules shows low-temperature ductility that compares very favorably to that which can be achieved in conventional material. Thus, a minimum transition temperature of 285°F was obtained in granule sheet tested in the as-rolled condition. This can be compared to transition temperatures of 320° and 350°F, which were obtained on two conventional commercial sheets after a 1-hr stress-relief anneal at 2190°F.

Annealing both types of materials at temperatures above 2190°F results in increasing their transition temperatures. However, as shown in Fig. 6, the magnitude of the increase in transition temperature of the "granule" sheet is much less than that obtained in the conventional commercial sheet made by powder metallurgy techniques. In fact, after annealing at temperatures above about 2400°F, the sheet prepared from granules shows consistently and significantly lower transition temperatures. This behavior is expected to be particularly advantageous for structures that must retain a maximum degree of low-temperature ductility after thermal cycling at temperatures in the range of 2600° to 3600°F. This improved performance results primarily from the unique mixed-grain structures that result on annealing over this temperature interval. In contrast, annealing the conventional sheet for 1 hr at 2910°F or greater produces a uniformly equiaxed structure, which has comparatively poor, low-temperature bend ductility.

Table 3 Effects of annealing temperature on grain growth in sheets of "granule" and conventional tungsten

1-hr annealing temperature, °F	New grains formed, % of original structure Granule sheet[a]	 Conventional commercial sheet[b]
1470–2190	0	0
2550	10–15	40–95
2910	15–20	100
3270	30–50	100
3630	50–95	100
4170	100	100

[a] Range of values from five sheets of slightly varying processing history.
[b] Range of values from two sheets of two different commercial sources.

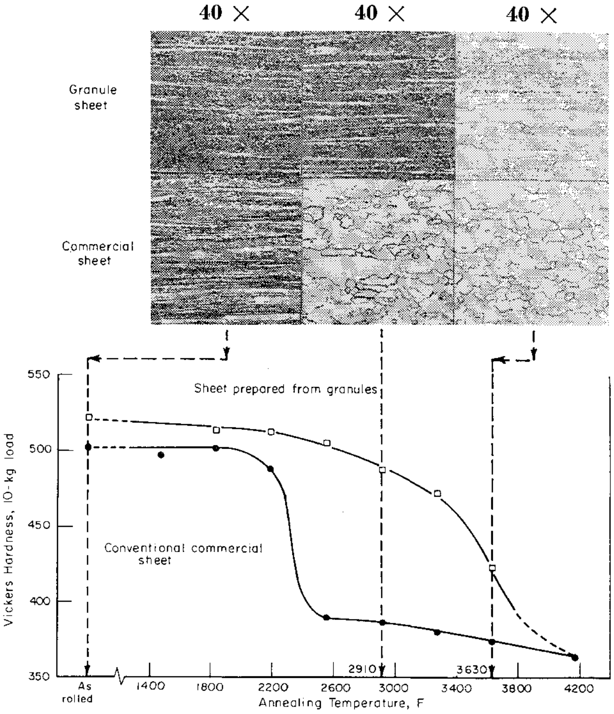


Fig. 5 Effect of 1-hr vacuum annealing treatments on structure and hardness of representative tungsten sheet samples, rolled through reductions of 95%.

Tensile Properties

Figure 7 summarizes the results of tensile tests on "granule" and conventional tungsten sheet, both after a 1-hr stress-relief anneal at 2190°F and a 1-hr anneal at 2910°F. The latter treatment was included to simulate the effect of high-temperature exposure.

Under both conditions of test, and especially after the high-temperature anneal, the "granule" sheet material shows an appreciable strength advantage over the conventional sheet. This margin decreases as temperature increases from 1000° to 3000°F but remains significant at 3000°F. It is expected

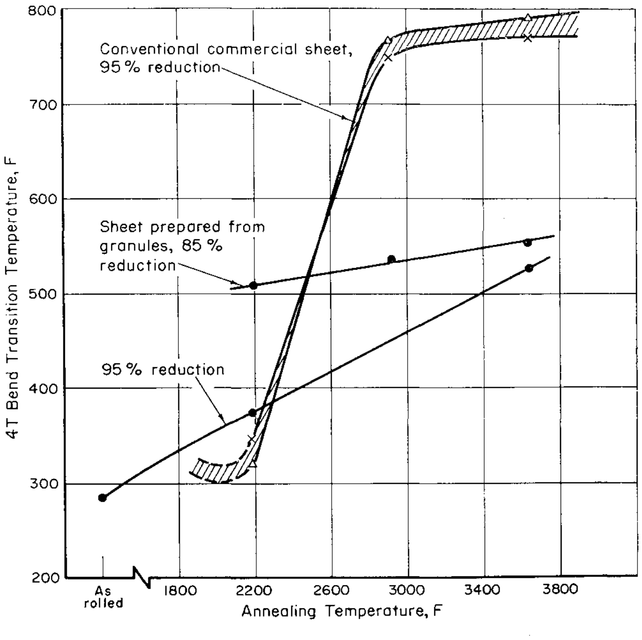


Fig. 6 Effect of 1-hr annealing treatments on the bend transition temperature of representative tungsten sheet samples.

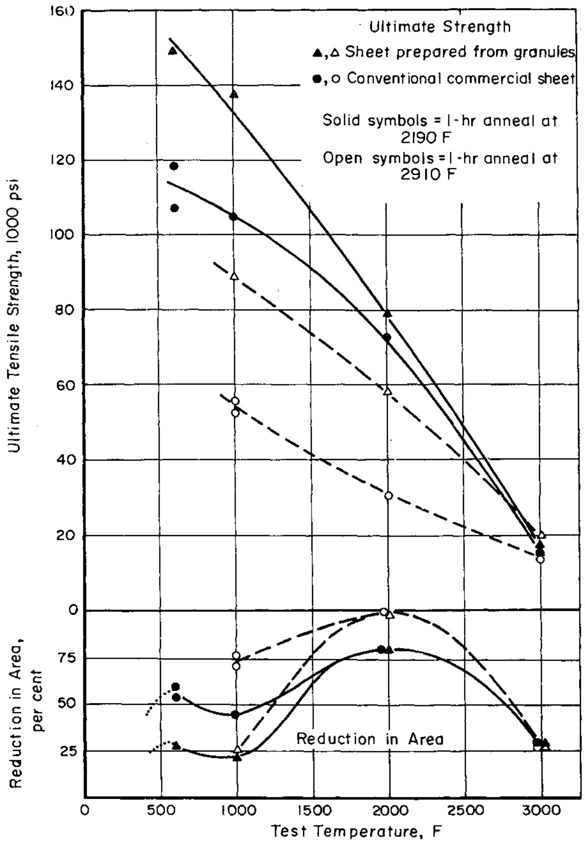


Fig. 7 Effects of annealing treatments and test temperature on tensile properties of representative tungsten sheet samples.

that the granule tungsten sheet will also show superior resistance to creep over this same range of temperatures.

At 600° and 1000°F, the strength advantage of the "granule" sheet is countered somewhat by its lower tensile ductility. However, at 2000° and 3000°F, identical ductility values were obtained for both types of material in both test conditions.

Future Prospects

The forementioned information, although preliminary in nature, demonstrates the unusual metallurgical characteristics of spherical tungsten granules made via the reduction of tungsten hexafluoride. This work further shows that these characteristics can be retained in massive shapes and sheet product through use of a gas-pressure bonding consolidation process. Sheet prepared from such material not only displays attractive combinations of strength and ductility as-prepared but retains these properties after cycling to extremely high temperatures as well.

The evaluation of other shapes consolidated from these tungsten granules is now in process at Battelle and elsewhere. This includes forging studies on massive billets as well as additional firing tests on experimental rocket nozzles of both high-density and infiltrated structures.

The high-purity granules are now available in experimental quantities, and appropriate action is being taken to satisfy demands for larger amounts of this material. Concurrent with the scale-up of production facilities, research is being continued to seek further improvements in the properties of the product.

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