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Bomford et al.

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[54] **THERMOMECHANICAL PROCESSING OF MECHANICALLY ALLOYED MATERIALS**

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[52] **U.S. Cl.** ..... **148/11.5 F**

[51] **Int. Cl.** **B22f 3/18**

[58] **Field of Search** ..... 148/11.5 F; 75/0.5 BB, 75/0.5 BC

[56] **References Cited**

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3,746,581	7/1973	Cairns et al.	148/11.5 F
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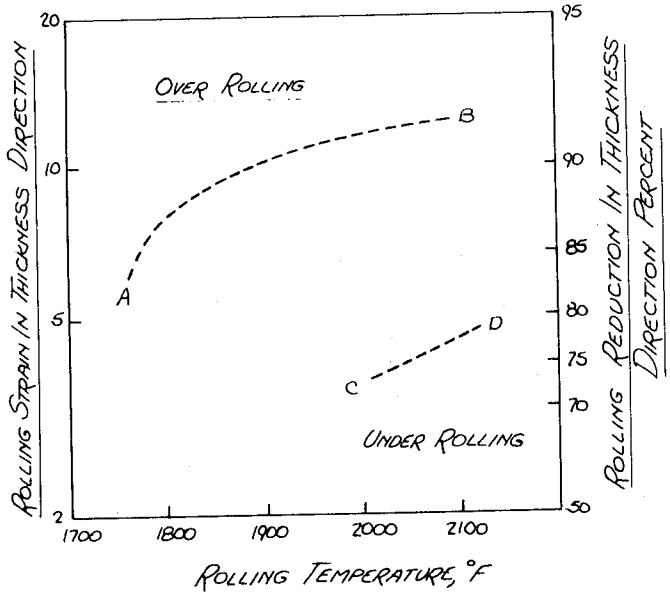
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[57] **ABSTRACT**

Flat rolled products are produced from mechanically alloyed composite particles by compaction and hot working using prescribed heat treatments, strain, strain rates, etc.

8 Claims, 2 Drawing Figures



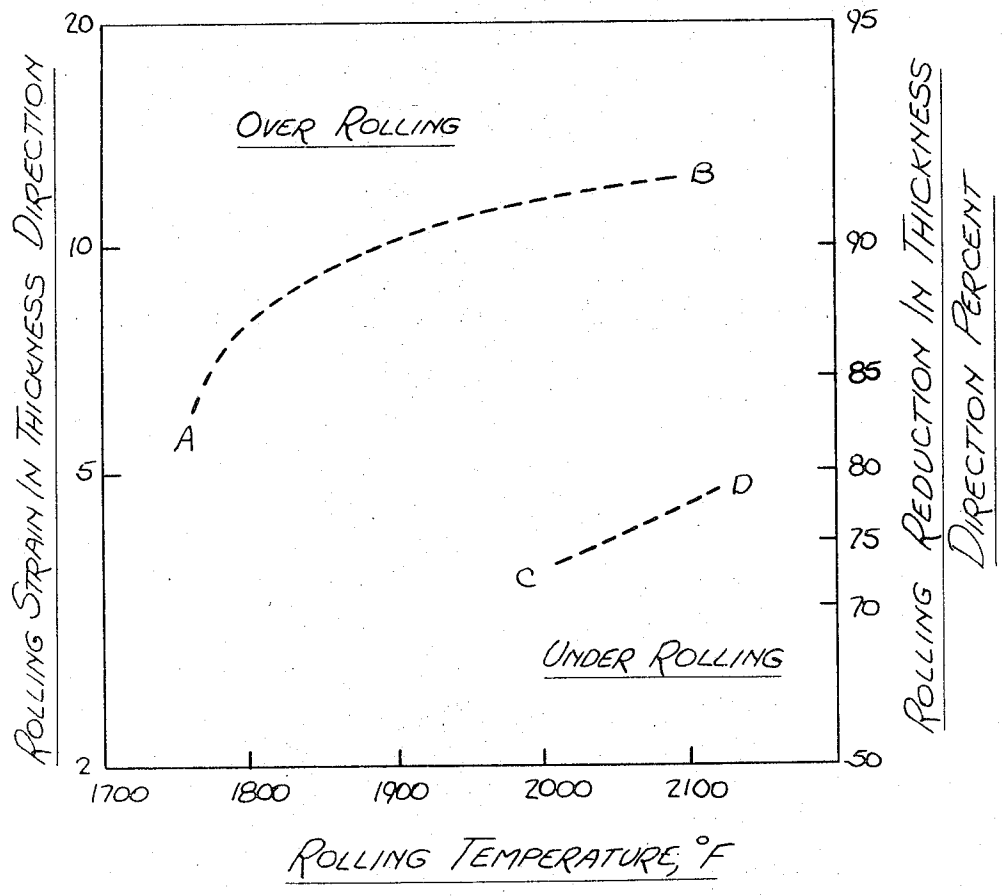

ROLLING STRAIN IN THICKNESS DIRECTION
ROLLING REDUCTION IN THICKNESS DIRECTION PERCENT
ROLLING TEMPERATURE, °F
OVER ROLLING
UNDER ROLLING
A
B
C
D
20
10
5
2
95
90
85
80
75
70
50
1700
1800
1900
2000
2100

Fig. 1.

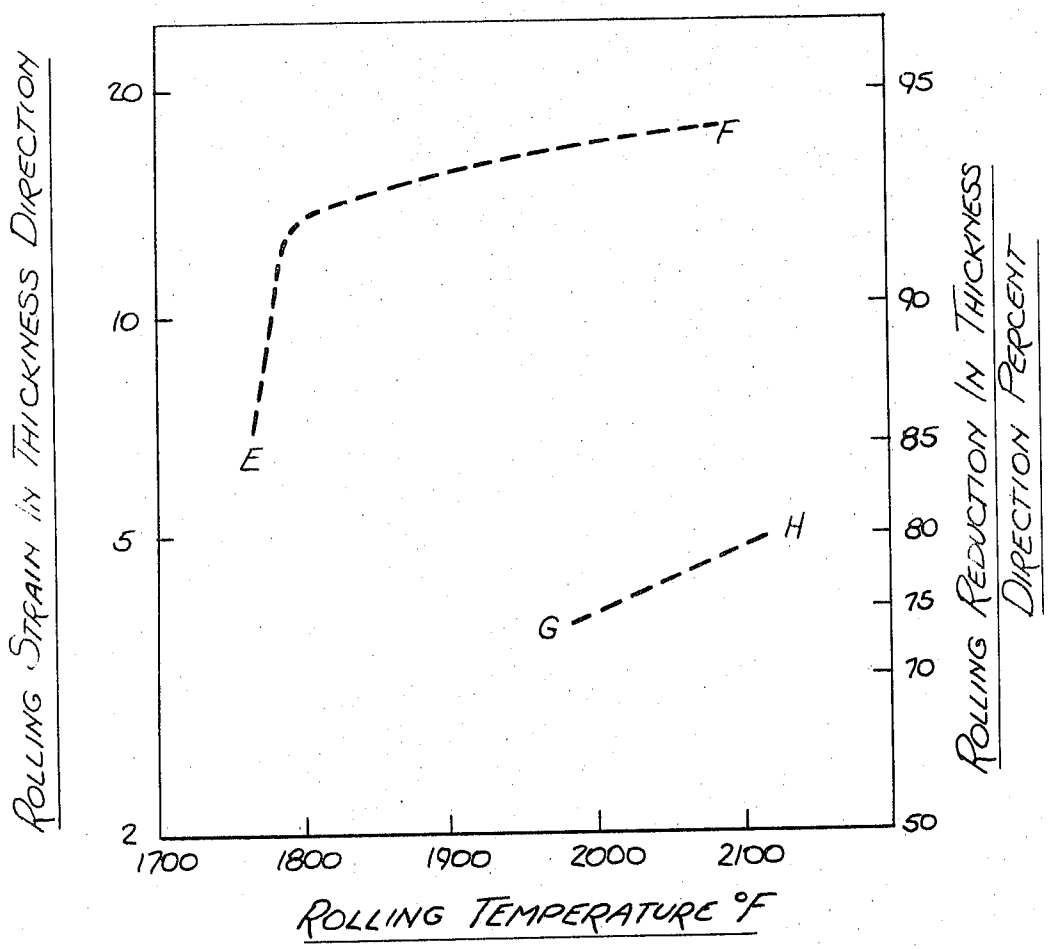

ROLLING STRAIN IN THICKNESS DIRECTION
20
10
5
2
95
90
85
80
75
70
50
E
F
G
H
1700
1800
1900
2000
2100
ROLLING TEMPERATURE °F
ROLLING REDUCTION IN THICKNESS DIRECTION PERCENT

Fig. 2.

THERMOMECHANICAL PROCESSING OF MECHANICALLY ALLOYED MATERIALS

The subject invention relates to powder metallurgy, and is particularly addressed to the fabrication of dispersion strengthened "mechanically alloyed" alloys, notably the superalloys.

The recently introduced concept of "mechanical alloying," described in U.S. Pat. Nos. 3,591,362 and 3,723,092, incorporated herein by reference, involves, as is known, the dry and intensive milling of powders in high energy machines and under special conditions during which constituent powders are repeatedly fragmented and cold bonded by the continuous impacting action of attriting elements. This processing is continued for a period such that composite product powder particles of saturation, or at least substantial saturation, hardness are formed, the composition of which correspond to the percentages of the respective components in the original charge. By reason of this, the constituent powders become most intimately interdispersed at close interparticle spacings, the composite particles being exceptionally dense and homogeneous, and characterized by cohesive internal structures. A further specific attribute of this unique development is that it permits of precipitation hardening, dispersion strengthening and matrix stiffening to be brought together in one alloy, particularly the nickel and nickel-chromium superalloys.

Virtually all of the thermomechanical processing of mechanically alloyed composite particles has been accomplished by recourse to extrusion, a seemingly indispensible and essential step. There are limitations attendant extrusion, however, and it would be of benefit to have at one's command such techniques as hot rolling to produce desired mill products, among which might be mentioned plate, strip, and sheet. In retrospect, it has probably been the anticipated difficulties expected in connection with hot rolling which may have rather self-mandated or at least encouraged turning to extrusion. This would not have been misplaced for we have found that a considerable number of parameters are involved in ultimately achieving an acceptable flat mill product such as those above-mentioned, including (i) the nature of the mechanically alloy composite particles (ii) compaction temperature, (iii) rolling temperature, (iv) percentage reduction (strain), (v) strain rate, (vi) product thickness, etc.

In any case, we have discovered that satisfactory flat products, including plate, strip, sheet and the like, can be produced from mechanically alloyed materials, provided that the processing parameters described herein are observed. Superalloy sheet having good stress rupture properties at elevated temperatures (1900°F.) has been produced, the sheet being of a thickness of but 0.02 inch. Moreover, these properties obtain in both the longitudinal and transverse direction. Needless to say, such characteristics greatly contribute to the production of gas turbine combustion, turbine and after burner components, applications requiring an alloy to be in sheet form and capable of withstanding the demands imposed by stress at high temperature.

Generally speaking, the present invention contemplates subjecting "mechanically alloyed" dispersion strengthened composite alloy particles to a processing sequence involving (i) compacting the composite particles at a temperature above 1,700° but less than 2,100°F., and most advantageously, over the range of about 1,850° to 2,000°F. and thereafter (ii) hot working as by rolling the compacted billet so produced at a temperature above the recrystallization temperature of the alloy and up to 2,050°F., with a temperature range of about 1,800° to 2,000°F. being deemed beneficial, the rolling operation being conducted at (iii) a strain rate of from about 3 to 4 up to 30 or 40 in/in/sec and with (iv) the total (both longitudinal and transverse) percentage reduction in thickness of the compact being at least 75 percent, preferably at least 80 percent, and up to 97 percent. To develop stress-rupture properties, the alloys are thereafter (v) heated at a temperature causative of germinative grain growth (secondary recrystallization) such that the alloys take on a structure comprised of course elongated grains and which is characterized by an absence of fine grains.

MECHANICALLY ALLOYED PARTICLES

Prior to the compaction step, milling of the powder undergoing mechanically alloying should be continued until cold worked composite metal powders are produced characterized by markedly increased hardness (that is, the powder contains a substantial amount of stored energy).

COMPACTION

Compacting of the mechanically alloyed particles can be accomplished by known means, including hot pressing, extruding using a blank die, press forging of loose powder in a box, etc. The point of concern is that an excessively high temperature, i.e., 2,100°F. and above, be avoided. High compaction temperatures tend to "anneal out" an undue amount of the composite particle energy imparted by way of the mechanical alloying phenomenon itself. This lends ultimately to products having an unnecessarily high amount of fine grains which in turn detract from stress-rupture strength. On the other hand, compaction temperatures below 1,700°F. can result in failure to achieve full densification or cold cracking in the compacted billet. While a temperature range of 1,750° to 2,050°F. may be employed it is much preferred to use a range of 1800° or 1850° to 2000°F.

HOT WORKING

a. Temperature

The working operation is preferably conducted by hot rolling. As is the case with compacting, should the rolling temperature be to the excess, i.e., 2050°F. and above, too much energy will be annealed out due to dynamic recovery during rolling. The rolling temperature should not exceed 2,050°F. and it is to advantage that it be maintained below about 1,950°F. This excessive recovery can also ensue from a combination of relatively high rolling temperature, say 2,000°F. and above plus a relatively high strain rate, e.g., about 15 or 20 in-/in/sec or more, which can induce further adiabatic heating in the material.

Should the rolling temperature be needlessly too low, then overworking, especially at higher working strain rates, too easily can be the result with a concomitant drop in properties. Too, the alloys tend to manifest a propensity toward or become more susceptible to cracking. A rolling temperature of 1,825° to 1,975°F. is deemed most satisfactory. It might be mentioned that alloys in the overworked state tend to recrystallize in an

equiaxed manner or to a fine grain size. On the other hand, a final state of underworking leads to an alloy which virtually will not undergo secondary recrystallization.

b. Strain rate

As above indicated, a strain rate of about 3 to 4 and up to about 30 or 40 in/in/sec is considered satisfactory. With strain rates below about 3 in/in/sec, it is considered that the imparted strain energy is somewhat balanced by dynamic recovery so that germanative grain growth will not take place. Strain rates much above about 40 in/in/sec tend to cause overworking at the lower working temperatures, or excessive adiabatic heating and recovery at the higher working temperatures. A strain rate of about 15 to about 30 in/in/sec is considered quite suitable.

c. Strain

The total reduction in thickness (strain) required is at least 75 percent. It has been found that in the absence of sufficient strain, recrystallization response upon the application of germinative grain growth treatment is impaired. Coarse grains were obtained but they were not elongated. To the other extreme, a total reduction in thickness much beyond 97 percent is an invitation to overrolling and attendant consequences. A total strain of about 80 to 91 percent reduction in thickness, (i.e., a log rolling strain of about 0.5 to 1.2) is decidedly of particular benefit.

d. Rolling temperature, strain and rolling direction

In striving for optimum results, it is to be emphasized that rolling temperature, strain and direction of rolling are not independent. Rather, they are interrelated. This is reflected by the curves in FIGS. **1** and **2,** the former being directed to unidirectional rolling with the latter involving cross rolling. It can be seen that a rolling temperature of 1,850°F. and a strain of 1.1 (approx. 90.5 percent reduction in thickness) is not recommended for unidirectional processing due to overrolling, although this combination would be generally acceptable for cross rolling. While the rolling temperature would be satisfactory in both instances, the strain would be unnecessarily high for unidirectional rolling. Accordingly, rolling temperature and strain should be related to strain so as to represent a point falling within the curves AB and CD of FIG. **1** and curves EF and GH of FIG. **2,** depending upon rolling direction.

e. Product Thickness

The products contemplated herein must be heat treated to develop the coarse elongated grain structure necessary for elevated temperature use. However, when the final thickness of the flat product to be produced is less than about 0.1 inch thick, then recrystallization should be induced prior to completion of the hot working. The reason for this is to prevent formation of elongated grains which would extend the full thickness of the material. Through thickness grain boundaries, so formed, are deleterious to strength and ductility of the sheet product. Incident to this, the compact billet should be hot reduced in thickness at least about 75 percent, preferably at least 80 percent, before the grain growth treatment is applied. Rolling is thereafter completed.

f. Heat Treatment.

The germinative grain growth treatment should be conducted at a temperature above about 2,200°F. and below the incipient melting temperature, depending upon the given alloy composition. A range of 2,350 to 2,450°F. will be generally quite satisfactory for most, if not all, superalloys. This will result in coarse elongated grains having aspect ratios above about 5:1, e.g., 10:1 to 50:1.

The following data are given as illustrative of the invention.

Dispersion strengthened, mechanically alloyed powder composite particles of Alloys Nos. **1** and **2,** Table I, were packed into cans, sealed and compacted at 1,900°F. to solid billets in an extrusion press using a blank die.

TABLE I

Alloy	Cr %	Al %	Ti %	Zr %	B %	Y_2O_3 %	Ni %
1	20	0.6	1.0	0.07	0.007	1.3	Bal.
2	20	1.2	2.4	0.07	0.007	1.3	Bal.

Bal. = balance nickel plus impurities
NOTE: nominal composition given

The billet-compacts were cog rolled to square and then rolled directly to plate or sheet, or were sectioned and ground to provide two parallel faces to which mild steel plate was welded. The billets and canned blocks were hot rolled to the various reductions and at the different temperatures reported in Tables II through IV. In producing the thinner sheets several plates stacked in a sealed mild steel container were rolled, (the container can be stainless steel, nickel or similar material). To prevent adhesion, the plates were separated from one another using Al_2O_3 powder (a suspension of glass or ceramic material may be used as the separation compound). The rolled sheets parted rather easily.

The rolled plates and sheets were then heat treated at 2,400°F. in an effort to achieve a coarsened, elongated structure and thus optimize stress-rupture properties. This treatment was applied after final rolling where the desired thickness was greater than 0.1 inch; otherwise, it was applied at an intermediate rolling stage to obviate having the grain boundaries completely transversing the product thickness.

Stress rupture strength and ductility were determined at **1900**°F. The criterion for an acceptable alloy product was an approximate 1,000 hour stress rupture life or higher at the 1,900°F. temperature under a stress of 10,000 psi.

EXAMPLE I

⅛-inch plate (perhaps more accurately sheet) was produced from Alloy **1.** The rolling schedule and properties are given in Tables II and III, respectively, the billet having been compacted at 1,900°F., with the starting thickness being 1½ inches.

TABLE II

Rolling Schedule		
Pass No.	Thickness Inches	
1	1⅛	Cross roll
2	¾	do.
3	½	Straight roll
4	⅜	do.
5	¼	do.
6	⅛	do.

NOTE: Longitudinal direction parallel to cylinder axis of compacted billets. Total rolling reduction approx. 91%.

TABLE III

Test	Rolling Temp. (°F.)	Longitudinal Stress (ksi)	Life (hours)	El. %	Approx. 1000 hr. Rupture (ksi)	Transverse Stress (ksi)	Life (hours)	El. %	Approx. 1000 hr. Rupture (ksi)
A	1800	<19	115.2*	2.2	16.5	<19	163.8*	1.8	18.5
		19	32.8			19	309.8*		
						20	40.5		
B	1900	<19	235.8*	2.2	18.5	<19	145.6	3.5	18.5
		19	262.7			19	469.8		
C	2000	<19	168.6*	2.7	19	<17	47.3*	1.8	14
		19	61.8			17	9.4		
D	2100	<18	163.0*	2.7	15	<17	189.6*	2.7	14
		18	15.1			17	24.4		

Mechanical Alloying Parameters:
Attritor: 100 gallon capacity
Speed: 75 rpm
Time: 22 hours
* Unbroken — stress raised

Regarding Table III, it will be observed that stress-rupture strength was quite high irrespective of rolling direction. The best combination of biaxial strength was obtained in connection with the 1,900°F. roll, although the 1,800°F. roll offered a higher transverse strength, with the 2,000°F. rolling temperature being more appropriate for the longitudinal test. Properties were markedly falling off in respect of the 2100°F. rolling temperature.

EXAMPLE II

This example illustrates production of thin sheet (0.05 inch).

Plate of ⅛-inch thickness was produced from Alloy 1 as described in Example I above. The plate was heat treated at 2400°F. for one-half-hour and the mild steel can pickled off. Three such plates were cut into 5" squares, stacked and sealed into a mild steel container. Al_2O_3 was used as parting compound. The piece was unidirectionally rolled to three-eighths inch thickness in two passes. At this point the sheets were about 0.05 - 0.06 inch thick. In Table IV there are given the results of tests at 1,900°F., three separate hot rolling temperatures being reported.

The stress-rupture strengths obtained in the longitudinal direction are rather noticably higher than those obtained in the transverse direction. It is considered that cross rolling during stack rolling would have minimized the disparity. In any event, the highest rupture strengths were obtained at rolling temperatures of 1,800° and 1,900°F.

EXAMPLE III

Following the general procedure of Example II, sheets about 0.020–0.03 inch thick were formed using Alloy 1 with the test data being reported in Table V. Again, quite satisfactory results were obtained.

TABLE V

Test	Rolling Temp. (°F.)	Stress (ksi)	Life (hours)	El. %	Approx. 1000 hr. Rupture (ksi)	Test Direction
H	1900	15	44.9	0.9	13	Longitudinal
		15	4.7	0.9	12	Transverse

Mechanical Alloying Parameters:
Attritor: 100 gallon capacity
Speed: 75 rpm
Tim: 22 hours

EXAMPLE IV

Plates of Alloy 2 were also prepared to a thickness of about one-fourth-inch for a total reduction in thickness of about 90 percent using three different rolling schedules as follows:

Schedule I

i. at 1950°F., 57 percent reduction in longitudinal direction, plus

ii. at 1950°F., 40 percent reduction in longitudinal direction, plus

TABLE IV

Test	Rolling Temp. (°F.)	Longitudinal Stress (ksi)	Life (hours)	El. %	Approx. 1000 hr. Rupture (ksi)	Transverse Stress (ksi)	Life (hours)	El. %	Approx. 1000 hr. Rupture (ksi)
E	1800	15	306.5*	1.8	16	15	92.2*	1.8	14
		16	121.1*						
		17	28.0*			16	23.8		
		18	51.3						
F	1900	15	547.7*	1.8	16	15	42.7*	0.9	13.5
		16	123.2*						
		17	27.9*			15	25.3*		
		18	49.9			16	14.4		
G	2000	15	69.2*	1.8	13.5	15	63.1	1.8	13.5
		15	154.0						

Mechanical Alloying Parameters:
Attritor: 100 gallon capacity
Speed: 75 rpm
Time: 22 hours
*Unbroken — stress raised.

iii. at 1950°F., 47 percent reduction in longitudinal direction, plus

iv. at 1950°F., 25 percent reduction in longitudinal direction.

Schedule II

i. at 1950°F., 42 percent reduction in longitudinal and 29 percent in transverse direction, plus

ii. at 1950°F., 40 percent reduction in longitudinal direction, plus

iii. at 1950°F., 47 percent reduction in transverse direction, plus

iv. at 1900°F., 25 percent reduction in longitudinal direction.

Schedule III

i. at 1800°F., 35 percent reduction in longitudinal direction, plus

ii. at 1800°F., 37 percent reduction in transverse direction, plus

iii. at 1800°F., 40 percent reduction in transverse direction, plus

iv. at 1800°F., 50 percent reduction in longitudinal direction, plus

v. at 1800°F., 23 percent reduction in longitudinal direction.

The sheet materials were heat treated for one hour at 2,400°F. for germinative grain coarsening and 24 hours at 1,300°F. for aging and thereafter tested for stress-rupture behavior at 1,900°F. Test results are set forth in Table VI, together with the rolling schedule and approximate total reduction in thickness.

TABLE VI

Test	Rolling Schedule	Total Reduction From Original Thickness		Overall Total Reduction in Thickness	Est. Total Reduction in Area	Estimated 1900°F., 100 Hr. Rupture Strength (ksi)	
		Long.	Trans.		Longitudinal	Long.	Trans.
I	I	90	0	90	85	12.9	10.9
J	II	73	17	90	80	10.7	10.9
K	III	50	62.5	92	78	—	12.5

Mechanical Alloying Parameters:

Attritor: 100 gallon capacity
Speed: 75 rpm
Time: 22 hours

Among the alloys to which the invention is applicable are those containing up to 65 percent, e.g., 1 to 25 or 35 percent, chromium; up to 30 percent, e.g., 5 to 25 percent, cobalt; up to 10 percent, e.g., 1 to 9 percent, aluminum, and up to 8 percent, e.g., 1 to 7 percent, titanium, particularly those alloys containing 6 percent or more of aluminum plus titanium; up to 30 percent, e.g., 1 to 8 percent molybdenum, up to 25 percent, e.g., 2 to 20 percent, tungsten, up to 10 percent columbium, and up to 10 percent tantalum, particularly those containing at least 4 percent or in total of Mo + W + Cb + Ta; up to 2 or 4 percent zirconium; up to 0.5 percent boron, up to 5 percent hafnium; up to 2 percent vanadium; up to 6 percent copper; up to 5 percent manganese, up to 70 percent iron; up to 4 percent silicon, and the balance essentially nickel. Cobalt-base alloys of similar composition can be treated. Superalloys and other contemplated alloys can contain up to, say, 10 percent or more by volume of a refractory dispersoid material including the oxides, carbides, nitrides and borides. Such refractory dispersoids can be of various elements including yttrium, lanthanum, thorium, zirconium, hafnium, titanium, silicon, aluminum, cerium, uranium, magnesium, calcium, beryllium and the like. As a practical matter, only a very small amount of such dispersoids need be employed, e.g., up to 5 percent by volume.

Finally, it will be understood that modifications and variations of the invention might be resorted to without departing from the spirit and scope thereof as those skilled in the art will readily understand. For example, appropriate annealing treatments can be employed during the overall hot working operation. Such are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for producing flat mill products from mechanically alloyed composite powder particles which comprises compacting the composite particles at a temperature within the range of about 1,700°F. to 2,100°F., hot rolling the compacted body at a temperature above the recrystallization temperature of the alloy but below about 2,050°F. and at a strain of from about 3 to about 40 in/in/sec, and continuing the hot rolling operation until the percentage reduction in thickness of the compacted body is at least 75 percent and up to 97 percent.

2. A process in accordance with claim **1** in which the compaction temperature is from 1,850° to 2,000°F.

3. A process in accordance with claim **1** in which the temperature of hot rolling is from 1,800° to 2,000°F.

4. A process in accordance with claim **1** in which the strain rate is about 15 to 30 in/in/sec.

5. A process in accordance with claim **1** in which the percentage reduction in thickness is from about 80 to about 91 percent.

6. A process in accordance with claim **1** in which if the hot rolling is accomplished unidirectionally, the rolling temperature and strain are correlated such as to represent a point within the curves AB and CD of FIG. 1 of the accompanying drawing and if the hot rolling is conducted in two directions, the rolling temperature and strain are correlated to give a point within the curves EF and GH of FIG. 2 of the drawing.

7. A process in accordance with claim **2** in which the hot rolling temperature is from 1,800° to 2,000°F., the strain rate is from about 15 to 30 in/in/sec and the percentage reduction in thickness is about 80 to about 91 percent.

8. A process in accordance with claim **7** in which the product is thereafter heat treated at a temperature from about 2,200°F. to below the incipient melting temperature of the alloy to achieve a coarse elongated grain structure.

* * * * *