This application is a continuation-in-part of our prior application Serial No. 327,115, filed Nov. 29, 1963, now abandoned.

This invention relates to processes for making metal sheet and to the product produced. More particularly the invention is directed to processes for producing a sheet of face-centered-cubic metal having a melting temperature of from 1000 to 1540° C., especially nickel, said sheet having a particular refractory oxide dispersed therein and having high strength at elevated temperatures, which processes include the steps of (1) consolidating to a solid body having a density above about 30% of theoretical density a powder of said metal in which there is substantially uniformly dispersed about from 0.01 to 5.0% by volume of refractory oxide particles having an average size of from 5 to 250 micrometers, said oxide having a free energy of formation at 1000° C. above 60 kilocalories per gram atom of oxygen and a melting point above 1000° C., (2) mechanically hot-working said solid body to a formed body having a length substantially greater than its width or thickness, (3) rolling said formed body, at a temperature not substantially higher than about 50% of its absolute melting point to effect a reduction of at least 30% in its thickness and form a sheet, and (4) heat-treating said sheet at above its recrystallization temperature but below its melting point for a time sufficient to effect recrystallization of the metal therein in a preferred crystallographic orientation.

The invention is further particularly directed to metal sheet which can be produced by processes of this invention and has high strength at elevated temperatures, said processes being describable, in one embodiment, as cold-worked, dispersion-hardened, face-centered-cubic metal sheet having a preferred crystallographic orientation, value-selected from the group of values consisting of (321) <121>, (200) <001>, (110) <112>, and (110) <001>, said orientation being so perfect as to have an angular deviation of no more than about 30° from each pole of the idealized orientation as measured on a stereographic projection at one half the maximum intensity value and being stable for at least one hour against appreciable change at temperatures up to 80% of the absolute melting temperature of the metal. Further particular embodiments will appear hereinafter.

It has been discovered, however, that the strength at elevated temperatures of certain face-centered-cubic metals such as nickel and its alloys can be substantially improved by dispersion therein of minor amounts of refractory metal oxides such as thoria. Alexander et al. Patent 3,087,234 describes certain of these novel systems and discloses that they may be prepared in powder form and the powder particles bonded together by hot-rolling or hot-extruding. In some instances, when this is attempted to form such dispersion-strengthened metals into sheet, problems are encountered in that the sheet cannot be bent around as small a radius as desired without having a tendency to crack. This tendency gives rise to problems of fabricability.

Now, according to the present invention it has been found that these problems of fabricability are resolved and sheet having unexpectedly great strength at elevated temperatures and having great ability to resist recrystallization and hence to retain high strength at high temperatures is produced by processes in which a face-centered-cubic metal such as nickel having a particular refractory oxide dispersed therein is consolidated to a solid body, this body is mechanically hot-worked, as by extrusion or forging, to a formed body having a length substantially greater than its width or thickness, the formed body is cold-rolled to a reduction of at least 30% in thickness to form a sheet, the sheet is heated to effect recrystallization of the metal therein in a preferred orientation, and optionally the recrystallized sheet is further rolled below its recrystallization temperature in a direction which does not substantially change this preferred orientation, to effect a further reduction of its thickness. For nickel initially hot-worked by extrusion the preferred orientation is (321) <121> in the recrystallized and finally rolled sheet and the direction of final rolling is perpendicular to the direction of extrusion; for nickel initially hot-worked by forging the preferred final orientation is (101) <001> and the direction of final rolling can be either parallel to or perpendicular to the direction of forging.

It has been further found that the novel metal sheet products which can be produced by the above-mentioned processes can be characterized by having a preferred crystallographic orientation of the above-mentioned class, by the orientation being stable for at least one hour against appreciable change at temperatures up to 80% of the absolute melting point of the metal, and by the orientation being so perfect as to have an angular deviation of no more than about 30° from each pole of the idealized orientation as measured on a stereographic projection at one half the maximum intensity value.

The starting material which is consolidated as the first step in a process of this invention can be any face-centered-cubic metal having a melting temperature of from 1000° to 1540° C. in which there is uniformly dispersed about from 0.01 to 5.0%, preferably 1.8 to 2.5%, by volume, of a particulate refractory oxide having a free energy of formation above 1000° C. above 60 kilocalories, and preferably above 105 kilocalories, per gram atom of oxygen and having a melting point above 1000° C. The average particle size of the refractory oxide is from 5 to 250 micrometers, preferably from 20 to 200 micrometers. Suitable refractory oxides are enumerated at column 3 of U.S. Patent 3,087,234 and of these thoria is particularly preferred. Face-centered-cubic metals will be understood to include the elemental metals nickel and copper as well as alloys thereof, and those alloys of iron and cobalt which are face-centered-cubic. Of these, nickel is especially suitable.

Any method with which the art is familiar and which is capable of giving the desired uniformity can be used for dispersing the refractory oxide in the metal. Methods described in U.S. Patent 3,087,234 have been found to give particularly good results, especially when the method of Example 2 of that patent is used to give a dispersion of thoria in nickel.

Having selected a suitable dispersion of refractory oxide in metal this material, in powder form, is consolidated to a solid body having a density upwards of 30%, preferably upwards of 60%, of the theoretical density. This can be done by methods shown in U.S. Patent 3,087,234, such as compacting the powder under pressure. The powder can also be rolled into a sheet.

The next step is to mechanically hot-work the solid body to a formed body having a length substantially greater than its width or thickness. This can be done by such common methods as extrusion, hot-forging, swaging and the like. By "hot-working" is meant that the working
3. is done at a temperature above about 50% of the absolute melting temperature. When a nickel billet is forged, for instance, the compact can first be canned, and the temperature preferably is in the range of 1200 to 2300° F., more preferably 1300 to 2200° F. When a nickel billet containing thorium is extruded the temperature is preferably in the range of 1000 to 2400° F., more preferably 1500 to 1750° F., and the reduction ratio is preferably from 2:1 to 13:1. The formed body produced in this step is preferably in the shape of a slab of rectangular cross section, but extruded rod or forged bar also answers the necessary description. Forging can be carried out in two or more stages if desired.

The formed body is then rolled, at a temperature not substantially higher than 50% of its melting point, to effect a reduction of at least 30% in its thickness to form a sheet or thin slab. With extruded slab the reduction in thickness effected by this step is preferably 30 to 70%. With forged slab, the reduction is preferably at least 85%. This product may be further rolled to a thinner gauge, as described below.

The direction of this rolling is important. The formed body should be rolled in the lengthwise direction. For extruded rod this will be in the direction of working, i.e., of extrusion. For forged slab it may be in the direction of forging or perpendicular thereto.

Having rolled the product to a heavy sheet, the sheet is then heat-treated above its recrystallization temperature but below its melting temperature (i.e., at 1000 to 2400° F. for extruded nickel, 1500 to 2600° F. for forged nickel) for a time sufficient to effect recrystallization of the metal therein. It is found that for sheet prepared as above described this recrystallization will produce a preferred crystallographic orientation in the product. By "preferred" is meant an ideal or predominant orientation or lattice alignment, as observed by crystallographic X-ray examination. Preferred orientation is also sometimes referred to as crystallographic texture.

The preferred orientation of the recrystallized sheet can be represented by an ideal orientation having Miller-Indices, as for example (321) <112>, the first of the numbers (321) indicating the crystallographic plane which is parallel to the plane of the sheet and the second number <112> indicating the crystallographic direction parallel to the rolling direction. The values (321) <112> are a preferred orientation found in sheet produced according to this invention from extruded billet; for sheet produced from forged billet, a preferred orientation is (100) <001>. Other preferred orientations are (110) <112> and (110) <001>. For a more complete description of preferred orientation in metal reference is made to Structure of Metals, C. S. Barrett, McGraw-Hill, 1952, chapters XVIII and XIX.

 Orientations can be determined by standard X-ray diffraction techniques using the well-known reflection method employing an X-ray diffractometer developed by Schulz. This method is described in Elements of X-ray Diffraction, B. O. Cullity, Addison-Wesley, 1956, pp. 290 to 295. Other accepted methods can, of course, be used.

After the metal in the thick sheet is recrystallized the sheet optionally is again rolled, at a temperature below its recrystallization temperature, to effect a further reduction in its thickness. It is necessary, according to this invention, that this rolling be done in a direction which does not substantially change the preferred orientation. For sheet rolled from extruded billet the direction of rolling preferably is the direction parallel to the length— that is, cross-rolling, whereas with sheet rolled from forged bar and having a (100) <001> preferred orientation, the rolling after recrystallization can be either in the direction parallel to the length or perpendicular thereto.

It will be understood that this final cold rolling can be carried on in a plurality of steps with intermediate annealing. With thick sheet rolled from extruded billet, for example, if greater than 70% reduction in thickness is desired in the final rolling, either the sheet should be given an intermediate anneal or the final rolling should be carried out simultaneously with a heat-treatment—that is, the rolling should be effected at a temperature high enough to effect stress-relief in the sheet being rolled but below that temperature at which any additional recrystallization will take place. Similarly, with recrystallized sheet rolled from forged slab, there should be an anneal or stress relief before rolling beyond 85% reduction in thickness.

The cold-worked, dispersion-hardened, fac centered-cubic metal sheet which can be produced by an above-described process and is a product of this invention can be characterized by having a preferred crystallographic orientation value selected from the group of values consisting of (321) <112>, (100) <001>, (110) <112> and (110) <001>. It can be further characterized by the fact that the preferred orientation is stable for at least one hour against appreciable change at temperatures up to 80% of the absolute melting temperature of the metal. Products of this invention can also be characterized by having a preferred crystallographic orientation so perfect as to have an angular deviation of no more than about 30°, preferably no more than 23° and more preferably no more than 17°, from each pole of the idealized orientation as measured on a stereographic projection at one half the maximum intensity value. It will be understood that the preferred orientation of the sheet of the invention is determined by X-ray diffraction techniques. The product of the technique is a complete map or "pole figure" of the distribution of grain or crystal orientations.

The angular deviation, in degrees, at half maximum of the distribution curve, is surprisingly low in the products of this invention. This small deviation is believed to account for the very high strength of the novel products at elevated temperatures.

The novel sheet products have remarkable strength, especially at high temperatures. In the preferred products the ultimate tensile strength is in excess of 18,000 pounds per square inch at 1800° F. The products have great ability to resist recrystallization, and this property contributes to retention of high strength at high temperatures.

The invention will be better understood by reference to the following illustrative examples:

**Example 1**

An 8" diameter billet of nickel containing dispersed thorium produced using thorium-containing nickel powder prepared according to a process described in Example 5 of U.S. 3,087,234 was prepared by hydrostatically compacting the powder at 60,000 p.s.i., and sintering the compacted billet at 2200° F. in dry hydrogen. The billet was then heated under argon, and extruded to a rectangular cross sectional slab at a 13 to 1 reduction ratio with the work piece temperature being 1750° F.

A portion of the extruded sheet (approximately 0.530" gauge) was tested for room temperature strength, and elevated temperature (1800° F.) strength; and was studied by X-ray diffraction to determine the preferred orientation. The extruded billet was cold-rolled to approximately 40% reduction in cross sectional area in a direction parallel to the extrusion direction, and a portion of the sheet tested in the same manner as described above.

The remaining portion of the sheet was heat treated for one hour at 2000° F. and was further processed according to the steps listed in Table 1, below. Results of tests at intermediate points and on the final sheet product are given. For each gauge, the first set of strength figures is in the longitudinal direction and the second is in the transverse direction, both with respect to the final rolling direction.
**Example 2**

Using nickel powder containing 2% by volume of dispersed thorium, produced according to Example 5 of the above referred-to U.S. Patent 3,087,234, an 8" billet, 22" in length was compacted and sintered. This canned billet was heated to 2200°F, and forged vertically to a 10% reduction. The billet was then turned on its side and forged to 6", rotated 90°, perpendicular to the forging plane, and again forged to produce a slab 1.6" thick x 26" long x 16" wide.

This forged slab was pickled in hot HNO₃ to remove the steel can, and the edges of the forged billet were cropped to sound material. The forged slab was then rolled to sheet according to the following rolling and annealing schedule:

- **Step 1:** The forged slab was heated to 1000°F, and rolled lengthwise to a thickness of 0.162" x 26" wide x length, a reduction of 90%.
- **Step 2:** The rolled sheet was annealed in vacuum for one hour at 2000°F to effect recrystallization of the nickel therein.
- **Step 3:** The annealed sheet of Step 2 was cold rolled to a thickness of 0.062", a reduction of 62%.
- **Step 4:** The cold rolled sheet was annealed in vacuum one hour at 2000°F.
- **Step 5:** The annealed sheet of Step 4 was again cold rolled, the resulting thickness being 0.044", a reduction of 34%.
- **Step 6:** The cold rolled sheet of Step 5 was again annealed in vacuum for one hour at 2000°F.

In carrying out the six steps which are listed above, samples were removed after Steps 2, 4, and 6, and tensile tests in directions longitudinal and transverse to the rolling direction were made. The results of these tests are listed in the table below:

**TENSILE TESTS ON FORGED AND ROLLED SHEET AT 1800°F.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ultimate Tensile Strength, p.s.i.</th>
<th>Elongation, percent</th>
<th>Ultimate Tensile Strength, p.s.i.</th>
<th>Elongation, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>After Step 2</td>
<td>15,500</td>
<td>9</td>
<td>15,500</td>
<td>0.500</td>
</tr>
<tr>
<td>After Step 4</td>
<td>15,300</td>
<td>8.5</td>
<td>19,700</td>
<td>6.00</td>
</tr>
<tr>
<td>After Step 6</td>
<td>17,000</td>
<td>7.6</td>
<td>20,000</td>
<td>8.62</td>
</tr>
</tbody>
</table>

**Example 3**

The preferred rolling schedule on the recrystallized sheet of Example 2 has been found to be as follows:

- **Step 1:** Cold roll to 63% reduction; stress relief anneal—one hour at 2000°F; cold roll to 33% reduction; and finally stress relief anneal at 2000°F for one hour.

The following table shows typical properties of a nickel sheet product produced by this preferred route.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>0.2% Yield Strength, p.s.i.</th>
<th>Ultimate Tensile Strength, p.s.i.</th>
<th>Percent Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temp</td>
<td>1800°F</td>
<td>50,000</td>
<td>65,000-70,000</td>
</tr>
</tbody>
</table>

In stress-to-rupture testing, these products are found to last over 20 hours at 2000°F and 7000 p.s.i.

We claim:

1. In a process for producing a sheet of face-centered-cubic metal, having a melting temperature of from 1000 to 1540°C, said sheet having a particular refractory oxide dispersed therein and having high strength at elevated temperatures, the steps comprising (1) consolidating to a solid body having a density above about 30% of theoretical density a powder of said metal in which there is substantially uniformly dispersed about from 0.01 to 5.0% by volume of refractory metal oxide particles having an average size of from 3 to 250 micromillimeters, said oxide having a free energy of formation at 1000°C above 60 kilocalories per gram atom of oxygen and a melting point above 1000°C, (2) extruding said solid body at from 1200 to 2400°F, to a formed body having a length substantially greater than its width or thickness, (3) rolling said formed body, at a temperature not substantially higher than about 50% of its absolute melting point to effect a reduction of at least 30% in its thickness and form a sheet, (4) heat-treating said sheet at above its recrys-
tallization temperature but below its melting point for a
time sufficient to effect recrystallization of the metal
therein in a preferred (321) <i>121</i> crystallographic
orientation, said orientation being so perfect as to have
an angular deviation of no more than about 30° from each
pole of the idealized orientation as measured on a stereo-
graphic projection at one half the maximum intensity
value, and (5) rolling said recrystallized sheet at a tem-
perature below its recrystallization temperature in a di-
rection perpendicular to the direction of the initial rolling
of said formed body, to effect a further reduction of its
thickness.

2. In a process for producing nickel sheet having a
particulate refractory oxide dispersed therein and having
high strength at elevated temperatures the steps compris-
ing (1) forming a billet of nickel powder in which there
is substantially uniformly dispersed about from 0.01 to
3% by volume of refractory metal oxide particles having
an average size of 5 to 250 millimicrons, said oxide hav-
ing a free energy of formation at 1000° C. above 60 kilo-
calories per gram atom of oxygen and a melting point
above 1000° C., (2) extruding said billet at from 1200 to
2400° F. to form a slab having a length substantially
greater than its width or thickness, (3) rolling said slab,
at a temperature not higher than 1000° F., in the direc-
tion of its length to effect a reduction of at least 30% in
its thickness and form a thick sheet, (4) heat-treating said
thick sheet at above 1000° F. but below its melting point
for a time sufficient to effect recrystallization of the nickel
therein in a preferred (321) <i>121</i> crystallographic
orientation, and (5) rolling recrystallized sheet at a tem-
perature below its recrystallization temperature and
in a direction perpendicular to the direction of initial
rolling of said slab to effect a further reduction of its
thickness.

3. In a process for producing nickel sheet having par-
ticulate thorium dispersed therein and having high strength
at elevated temperatures the steps comprising (1) form-
ing a billet of nickel powder in which there is dispersed
about 1.8 to 2.2% by volume of thorium particles having
an average size of about from 20 to 200 millimicrons, (2)
forging said billet at from 1200 to 2300° F. to form a slab
of substantially rectangular cross section, (3) rolling said
slab at not higher than 1000° F. to effect a reduction of at
least 85% of its thickness and form a thick sheet, (4)
heat-treating said thick sheet at from 1500 to 2600° F. for
a time sufficient to effect recrystallization of the nickel
therein in a preferred (100) <i>001</i> crystallographic
orientation, said orientation being so perfect as to have
an angular deviation of no more than about 30° from
each pole of the idealized orientation as measured on a
stereographic projection at one half the maximum inten-
sity value, and (5) rolling said recrystallized sheet at a
temperature below its recrystallization temperature to
effect a further reduction of its thickness.

4. In a process for producing nickel sheet having par-
ticulate thorium dispersed therein and having high strength
at elevated temperatures the steps comprising (1) form-
ing a billet of nickel powder in which there is dispersed
about 1.8 to 2.2% by volume of thorium particles having
an average size of about from 20 to 200 millimicrons and
heating the billet in dry hydrogen at about 2200° F., (2)
extruding said billet at from 1200 to 2400° F. and a reduc-
tion ratio of from 2:1 to 13:1 to form a slab of substan-
tially rectangular cross section, (3) rolling said slab in
the direction of extrusion at not higher than 1000° F. to
effect a reduction of from 30 to 70% in its thickness and
form a heat-treatment thick sheet, (4) heat-treating said
thick sheet at from 1000 to 2400° F. for a time sufficient
to effect recrystallization of the nickel therein in a pref-
ere (321) <i>121</i> crystallographic orientation, said orienta-
tion being so perfect as to have an angular deviation of
no more than about 30° from each pole of the idealized
orientation as measured on a stereographic projection at
one half the maximum intensity value, and (5) rolling said
crystallized sheet in a direction perpendicular to the
direction of initial rolling of said slab at a temperature
below the recrystallization temperature of the sheet to
effect a further reduction of its thickness.

5. A cold-worked, dispersion-hardened, face-centered-
cubic metal sheet having a (100) <i>001</i> preferred crys-
tallographic orientation, said orientation being so perfect
as to have an angular deviation of no more than about
30° from each pole of the idealized orientation as mea-
sured on a stereographic projection at one half the max-
imum intensity value and being stable for at least one
hour against appreciable change at temperatures up to
80% of the absolute melting temperature of the metal.

6. Cold-worked nickel sheet having dispersed substan-
tially uniformly therein about 0.01 to 5% by volume of
refractory metal oxide particles having an average size of
5 to 250 millimicrons, said oxide having a free energy of
formation at 1000° C. above 60 kilocalories per gram
atom of oxygen and a melting point above 1000° C., the
nickel in said sheet having a preferred (321) <i>121</i>
crystallographic orientation, such orientation being so per-
fect as to have an angular deviation of no more than about
30° from each pole of the idealized orientation as mea-
sured on a stereographic projection at one half the max-
imum intensity values.

7. Cold-worked nickel sheet having dispersed substan-
tially uniformly therein about from 1.8 to 2.2% by vol-
ume of thorium particles, the nickel in said sheet having a
preferred crystallographic orientation of (321) <i>121</i>,
said orientation being so perfect as to have an angular
deviation of no more than about 23° from each pole of
the idealized orientation as measured on a stereographic
projection at one half the maximum intensity values.

8. Cold-worked nickel sheet having dispersed substan-
tially uniformly therein about from 1.8 to 2.2% by vol-
ume of thorium particles, the nickel in said sheet having a
preferred crystallographic orientation of (100) <i>001</i>,
such orientation being so perfect as to have an angular
deviation of no more than about 23° from each pole of
the idealized orientation as measured on a stereographic
projection at one half the maximum intensity values.

9. Cold-worked nickel sheet having dispersed substan-
tially uniformly therein about from 0.01 to 5% by volume of
refractory metal oxide particles having an average size of
5 to 250 millimicrons, said oxide having a free energy of
formation at 1000° C. above 60 kilocalories per gram
atom of oxygen and a melting point above 1000° C., the
nickel in said sheet having a preferred (321) <i>121</i>
crystallographic orientation, said orientation being so per-
fect as to have an angular deviation of no more than about
30° from each pole of the idealized orientation as mea-
sured on a stereographic projection at one half the max-
imum intensity value and being stable for at least one
hour against appreciable change at temperatures up to
80% of the absolute melting temperature of the nickel.

10. Cold-worked nickel sheet having dispersed substan-
tially uniformly therein about from 1.8 to 2.2% by vol-
ume of thorium particles having an average size of 20 to
200 millimicrons, the nickel in said sheet having a pre-
ferrated crystallographic orientation of (321) <i>121</i>,
said orientation being stable for at least one hour against
appreciable change at temperatures up to 80% of the
absolute melting temperature of the nickel.

11. Cold-worked nickel sheet having dispersed substan-
tially uniformly therein about from 1.8 to 2.2% by vol-
ume of thorium particles having an average size of 20 to
200 millimicrons, the nickel in said sheet having a pre-
ferrated crystallographic orientation of (321) <i>121</i>,
said orientation being so perfect as to have an angular
deviation of no more than about 30° from each pole of
the idealized orientation as measured on a stereographic
projection at one half the maximum intensity values.
atom of oxygen and a melting point above 1000° C., the nickel in said sheet having a preferred (100) <001> crystallographic orientation, such orientation being so perfect as to have an angular deviation of no more than about 30° from each pole of the idealized orientation as measured on a stereographic projection at one half the maximum intensity values.