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DISPERSION-STRENGTHENED NICKEL PRODUCED FROM ULTRAFINE COMMINUTED POWDERS

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16. Abstract

An investigation conducted to produce dispersion strengthened products by a mechanical comminution and blending approach was combined with a study of the effect of varying degrees of thermomechanical processing on the strength of the materials produced. Dispersion strengthened nickel products comparable or better in strength to the best available commercial products were produced. While the products generally increased in strength with increased amounts of thermomechanical processing, changes in composition of the composite were shown to affect the response of the material to the working process.

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DISPERSION-STRENGTHENED NICKEL PRODUCED

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SUMMARY

This investigation was conducted to determine whether dispersion strengthened materials, comparable in strength to the best commercial products (prepared by chemical approaches), could be produced by thermomechanical processing of comminuted and blended composites.

Nickel - 4 volume percent thoria, nickel oxide - 4 volume percent thoria, nickel - 0.5 volume percent zirconium - 4 volume percent thoria, and nickel - 2 volume percent aluminum oxide composites were prepared by mechanical comminution and blending of powders. The products were then cold pressed, sintered, hot rolled, and subjected to seven, 14, or 21 cold-roll - anneal cycles to develop the strength of the material. A purchased commercial nickel - 3 weight percent thoria powder was processed in the same manner for use as a reference. A number of the sheet materials produced were stronger in the 2000° F (1100° C) tensile and stress-rupture properties than both the processed reference powder and the best available commercial dispersion-strengthened nickel sheet product.

The strengths of the dispersion products produced in this investigation generally increased as the number of cold-roll - anneal cycles increased from seven to 21. This was true of the nickel - 4 volume percent thoria and the nickel oxide - 4 volume percent thoria products as well as the nickel - 3 weight percent standard. However, the nickel - 0.5 volume percent zirconium - 4 volume percent thoria product was strongest after seven cycles, and its strength decreased with more cycles. Thus addition of the zirconium appeared to change the response of the material to the cold-roll - anneal cycles and permit the development of greater strength with less thermomechanical processing.

INTRODUCTION

Efforts to develop dispersion strengthened materials with high melting point metal matrices have been under way for more than 20 years. During this time the most suc-

cessful high temperature dispersion-strengthened materials produced have been nickel or nickel base materials (containing ThO_2 dispersions) that have been made by chemical methods (refs. 1 and 2). Curently, commercial products, Thoria Dispersed Nickel (TD-Ni) and TD Nickel-Chromium (TD-NiC), are produced by the Fansteel Metallurgical Corporation.

Many methods other than chemical have been used in attempts to produce high strength dispersion products. The most frequently used method has been mechanical comminution and blending. The bulk of the efforts of the NASA-Lewis Research Center in the dispersion strengthening field has been concerned with this approach. This study is the latest of a series of investigations leading to the production of high strength mechanically produced dispersion-strengthened products.

It was recognized that if a mechanical blending and comminution approach were to successfully produce high strength products, fine submicron starting powders of metal and oxides would be necessary. Such powders were achieved by ball milling processes (ref. 3). Initial experiments were made to develop high strength Ni-MgO products from these powders (ref. 4). This study revealed inherent problems associated with producing high strength materials by this process:

(1) To permit control of processing steps, it was necessary to observe the distribution of the oxide in the starting blends. This was impossible to do using available electron miscroscopy techniques. To solve this problem two methods were developed for examining the starting blends. These methods are described in references 5 and 6.

(2) The impurity pickup during processing occurred and was believed to contribute to agglomeration of the intentionally added dispersoids. A practical solution to the problem is presented in reference 7. A useful equation to predict the interparticle spacing of oxide particles obtainable from the starting metal and oxide powders was also developed (ref. 8). This equation related the interparticle spacing of the oxide with the particle size of the matrix and oxide and volume fraction of the oxide. Using the experimental procedures described and the analytic work as well, a method was devised to produce nickel dispersoid bearing materials with microstructural parameters comparable to those of the best dispersion strengthened materials (ref. 7).

(3) The remaining problem, associated with producing strong dispersion strengthened nickel materials was that of thermomechanical working. The purpose of this additional processing is to produce a microstructure that would be stable and give the material strength at 2000° F (1100° C). Thermomechanical working procedures (such as extrusion, swaging, rolling, and annealing) which have successfully produced high strength dispersion-strengthened nickel in chemically produced products are given in references 1 and 2.

which have successfully produced high strength dispersion-strengthened nickel in chemically produced products are given in references 1 and 2.

The objective of this investigation was to determine whether dispersion strengthened products, comparable in strength to the best commercial materials, could be produced by thermomechanical processing of consolidated comminuted and blended products. A secondary objective was to try some variations in composition and powder processing to determine whether such changes would influence the response of the composite product to the thermomechanical treatment. Several types of composite materials were prepared by the mechanical comminution of powders. These consisted of nickel - 4 volume percent thoria (Ni-4ThO$_2$), nickel - 0.5 volume percent zirconium - 4 volume percent thoria (Ni-0.5Zr-4ThO$_2$), and nickel - 2 volume percent aluminum oxide (Ni-2Al$_2$O$_3$). The Ni-4ThO$_2$ products were also prepared by starting with NiO rather than nickel. Slabs of the consolidated powders were thermomechanically worked. As a reference for comparison, commercial, chemically prepared nickel - 3 weight percent thoria (Ni-3ThO$_2$) powder was processed in the same manner as the mechanically comminuted blends. Tensile and stress-rupture tests at 2000° F (1100° C) and microscopy studies were made of the final consolidated and worked products. A commercially available Ni-2ThO$_2$ sheet, tested in the as-received condition, was also used as a reference.

MATERIALS AND PROCEDURES

Materials

The raw materials used in the investigation were powders of nickel, nickel oxide (NiO), zirconium hydride (ZrH$_2$), thorium dioxide (ThO$_2$), aluminum oxide (Al$_2$O$_3$), commercial nickel - 3 weight percent thoria, and commercial sheet of nickel - 2 volume percent thoria. The source, form, size, grade, and purity of the materials are shown in table I.

The Ni-3ThO$_2$ was a composite powder made by Sherritt Gordon Mines, Ltd. and was obtained for processing into sheet material by methods developed at NASA. It was used as a reference material as was the Ni-2ThO$_2$ commercial TD-Ni sheet. The TD-Ni material is now available from the Fansteel Metallurgical Corporation, which recently acquired the DuPont facilities for production of dispersion-strengthened materials. The commercial materials are prepared by combinations of chemical coprecipitations with selective decomposition in some cases in the presence of colloidal ThO$_2$ particles.

TABLE I. - MATERIALS

Material	Form and size	Source and grade	Purity[a]
Raw Material			
Ni	Powder, 2.5μm	International Nickel Co. Inco B carbonyl powder	99.7 Ni
NiO	Powder, 0.2μm	Fisher Scientific Co. reagent grade	99.8 NiO
ZrH_2	Powder, 5.0μm	Metal Hydrides Div. of Ventron Corp.	97.8 ZrH_2
ThO_2	Powder, 0.03μm	Thorium Limited Co.	99.8 ThO_2
Al_2O_3	Powder, 0.03μm	Cabot Corp. Alon C	99.8 Al_2O_3
Commercial reference materials			
Ni-3 w/o ThO_2	Powder, 0.2-0.5μm	Sherritt Gordon Mines, Ltd. D.S. Nickel	
Ni-2 v/o ThO_2	Sheet, 0.030 in. (0.08 cm)	DuPont-Fansteel TD nickel	

[a]Suppliers' analysis.

Procedure

An abbreviated outline of the general processing steps used at NASA-Lewis is given in table II. The blends prepared for processing, the final products fabricated, and the

TABLE II. - GENERAL PROCESSING STEPS

Preparation of fine powder blend
     Grind matrix in heptane - 10 vol. % alcohol or water for 96 hr
     Add dispersoid and grind an additional 24 to 48 hr

Densification
     Heat powder to 600° F (300° C) in purified H_2 and hold for 2 hr
     Cold press powder into slabs (1 by 3 by 0.15 inches or 2.5 by 7.5
         by 0.4 cm) at nominally 8000 psi (56 MN/m^2) under argon
     Cold press slabs at 70 000 psi (490 MN/m^2) in isostatic press
     Heat slabs to 2000° F (1100° C) in H_2 and hold for minimum of 2 hr

Thermomechanical work
     Hot roll two passes at 30 percent reduction per pass at 2000° F
         (1100° C)
     Cold roll seven, 14, or 21 passes at 10 percent reduction per pass
         (with intermediate anneals of 30 min at 2200° F (1200° C) in H_2)

reference materials used are listed in table III. The letters NAS-CAB have been used to designate the NASA comminuted and blended products. The NAS-CAB products will hereinafter be identified by their blend compositions (in vol. %) as $Ni-4ThO_2$, $NiO-4ThO_2$ (heptane or water), $Ni-0.5Zr-4ThO_2$, and $Ni-2Al_2O_3$. It should be understood that the matrices of the final products are metallic in all cases. The commercial reference materials are (in wt. %) $Ni-3ThO_2$ (processed powder) and (vol. %) $Ni-2ThO_2$ (as-received sheet).

TABLE III. - COMPOSITIONS STUDIED AND COMMINUTION

AND BLENDING PROCESSES

Nominal compositions	Blends prepared for processing
Comminuted and blended	
$Ni - 4ThO_2$ (4.4 wt. %)	Direct grinding of Ni and ThO_2 in heptane-alcohol or heptane-oleic acid
$Ni - 0.5Zr - 4ThO_2$ (4.4 wt. %)	Grinding of Ni, ZrH_2, and ThO_2 in heptane-alcohol
$Ni - 4ThO_2$ (4.4 wt. %)	Grinding of NiO and ThO_2 in water
$Ni - 2 Al_2O_3$ (0.9 wt. %)	Direct grinding of Ni and Al_2O_3 in heptane-alcohol
Reference materials	
$Ni-3ThO_2$ (2.7 vol. %)	Densified and thermomechanically worked
$Ni - 2ThO_2$ (2.25 wt. %)	Tested in as-received condition

Grinding

All powders of nickel or nickel oxide were ground in a attritor in a heptane - 10-percent-ethyl alcohol medium for 96 hours (see table III). Either 4 volume percent ThO_2 or 2 volume percent Al_2O_3 was added to the slurries and grinding was continued for another 24 to 48 hours. Nickel balls, a nickel stirrer, and a nickel container were utilized to avoid contamination of the powders. During grinding an argon blanket was used over the top of the slurries to inhibit oxidation of the powders.

In one experiment 0.5 percent zirconium as the hydride was added to the nickel at the start of the grind. Also one $Ni-4ThO_2$ blend was ground with 10 percent oleic acid in the heptane instead of alcohol, and one $NiO-4ThO_2$ blend was ground in distilled water.

After grinding, the contents were dumped onto a screen and then washed through with the grinding liquid in order to separate the slurry from the grinding balls. The grinding and wash liquids were then evaporated at room temperature to a low volume in a hood and

the powder maintained in a concentrated slurry form until it was to be used.

The commercial Ni-3ThO$_2$ powder was consolidated in the as-received condition without prior grinding.

Densification and Sintering of Specimens

When ready for use, the remainder of the liquid was evaporated from the concentrated slurries to obtain the powders. In order to cold compact the powders, they were first annealed at low temperature. This was done by heating in hydrogen for 2 hours at 600° F (315° C). Twenty to thirty grams of powder were then cold pressed into a slab shape approximately 1.0 by 3.0 by 0.15 inch (2.5 by 7.5 by 0.4 cm) in an argon filled dry box at a nominal load of 8000 psi (56 MN/m^2). The slabs were then sealed in flexible plastic sheet and cold pressed isostatically at 70 000 psi (490 MN/m^2). The pressed pieces were cleaned and sintered by raising the temperature slowly in hydrogen to 2000° F (1100° C). The heating rate was controlled so that the monitored moisture level was maintained below 100 ppm. The heating rate was nominally 200° F per hour and the time required at 2000° F (1100° C) was between 2 and 8 hours. During the operation NiO is selectively reduced to Ni. At the completion of this operation the density was approximately 80 to 85 percent. Details of the method are given in reference 7.

Thermomechanical Working

With slight modifications the general procedures of reference 2 were utilized for the thermomechanical working process of this investigation. The partially densified slabs (0.1 to 0.2 in. or 0.25 to 0.50 cm thick) were heated in hydrogen and were given two hot rolls at 2000° F (1100° C) with reductions of about 30 percent each so that the total hot reduction was approximately 50 percent. The hot rolling was done on a four-high Loewy mill with $2\frac{1}{2}$ inch (6.4 cm) diameter by 8 inch (20 cm) long working rolls at a surface speed of 270 feet (82.4 m) per minute. After this treatment the density was close to theoretical. This was followed by seven, 14, or 21 cold rolling reduction passes of about 10 percent each with intermediate anneals (after each pass) of 30 minuted in hydrogen at 2200° F (1200° C). The cold rolling was performed in a four-high Fenn mill with the same dimensions as on the hot rolls on the working rolls at a surface speed of 5 feet (1.4 m) per minute. Final total reductions of the sheet material ranged from 74 to 93 percent. The final thickness of specimens ranged from 5 to 40 mils (0.013 to 0.10 cm) depending on the number of passes. In all cases a certain amount of edge cracking occurred in the hot and cold rolling. In most cases the edges could be trimmed and the rolling continued.

However, enough sheets were rolled so that test specimens were obtained for all combinations of matrix, oxide, and grinding media which were used as variables in the experiments.

Testing

As-rolled sheet specimens were tensile and stress rupture tested. Specimens were examined visually and the surfaces were sufficiently good so that they could be tested in the as-rolled condition.

The specimen configuration used in tensile-rutpure tests is shown in figure 1.

All the composite materials processed were screened by tensile testing at 2000° F (1100° C). Tensile tests were run at a crosshead rate of 0.02 inch (0.05 cm) per inch per minute and were made on sheet specimens that had received seven, 14, or 21 cold-
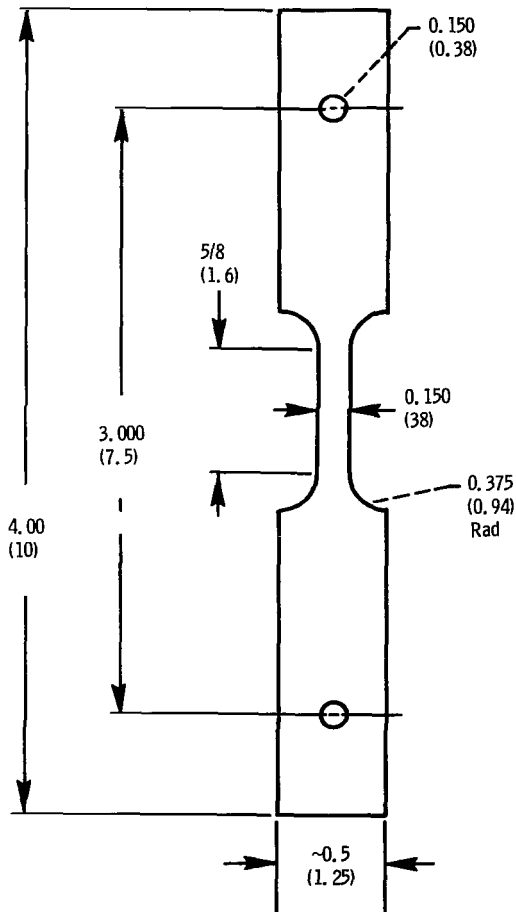
Figure 1. - Specimen configuration. (All linear dimensions are in inches (cm).)

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roll - anneal cycles. This strain rate is commonly used in this field and permits comparison with other results in the literature. In a number of cases 2000° F (1100° C) stress rupture tests were also performed. All tensile and stress rupture tests were performed in a vacuum of approximately 10^{-5} torr.

Metallographic Examination

Electron micrographic studies of several materials were made using conventional replication. In some cases thin foil and extraction techniques were also used.

TENSILE TESTS RESULTS AT 2000° F (1100° C)

Tensile test results at 2000° F (1100° C) are given in table IV and figures 2 to 7. In the figures the tensile strengths of the dispersion strengthened nickel materials are plotted against the number of cold-roll intermediate anneal cycles. It has been noted previously that hot rolling proceded the cold-roll - anneal cycles.

Reference Materials

Specimens of a fully fabricated commercial product, TD Ni-$2ThO_2$, and a product fabricated at NASA-Lewis from purchased commercially produced composite powder, Ni-$3ThO_2$, were tested as standards for comparison with the NASA comminuted and blended materials. In the case of the sheet specimens prepared from the purchased Ni-$3ThO_2$ powder, the material was processed in the same manner as the NASA prepared composites.

The results for the 30-mil (0.08-cm) TD Ni-$2ThO_2$ sheet tested in the as-received condition are shown at the bottom of table IV and figure 2. The 2000° F (1100° C) tensile results obtained are 9500 and 11 500 psi (66.5 and 80 MN/m^2). This material was obtained from a lot produced prior to 1967 and the working sequence is not known. The 2000° F (1100° C) tensile strength of TD Ni-2ThO2 sheet currently produced is reported in a Fansteel brochure to be 14 000 psi (98 MN/m^2) (ref. 10).

The tensile strengths of the products prepared from the Ni-$3ThO_2$ powder, also shown in figure 2, increased from an average (middle of the scatter band) tensile strength of 10 500 psi (73.5 MN/m^2) after seven cold-roll - anneal cycles to an average of 15 500 psi (108 MN/m^2) after 21 cold-roll - anneal cycles. Relatively reproducible test data were obtained. Specimen elongation ranged from 4 to 5 percent. The results are comparable

TABLE IV. - 2000° F (1100° C) TENSILE TEST DATA FOR

DISPERSION STRENGTHENED NICKEL SHEET MATERIAL

PREPARED FROM VARIOUS BLENDS

Material	Cold-roll anneal cycles					
	7		14		21	
	Tensile strength					
	psi	MN/m^2	psi	MN/m^2	psi	MN/m^2
Ni-3ThO$_2$ (reference)	9 500	66	12 500	87.5	15 000	105.0
	------	-----	13 500	94.5	15 500	108.5
	10 000	70.0	13 500	94.5	16 000	112.0
	11 000	77.0	13 500	94.5	16 000	112.0
	12 000	84.0	14 500	101.5	16 000	112.0
Ni-4ThO$_2$	5 500	38.5	11 500	80.5	16 500	115.5
	7 000	49.0	------	-----	20 500	143.5
	7 500	52.5	------	-----	------	-----
	8 500	59.5	------	-----	------	-----
NiO-4ThO$_2$ (heptane-alcohol grind)	19 000	133.0	20 500	143.5	21 500	150.5
			24 000	168.0	26 000	182.0
NiO-4ThO$_2$ (water grind)	4 500	31.5	16 500	115.5	16 500	115.5
	5 000	35.0	------	-----	19 000	133.0
	7 500	52.5	------	-----	------	-----
Ni-0.5Zr-4ThO$_2$[a]	16 500	115.5	16 000	112.0	12 500	87.5
	17 000	119.0	------	-----	13 000	91.0
	17 500	122.5	------	-----	13 500	94.5
	18 500	139.5	------	-----	14 000	98.0
	20 500	143.5	------	-----	15 000	105.0
	22 500	157.5	------	-----	------	-----
Ni-2Al$_2$O$_3$	8 000	56.0	12 500	87.5	[b]11 000	77.0
	11 500	80.5	14 000	98.0	[b]12 500	87.5
TD Ni-2ThO$_2$	Tested in as-received condition; work schedule unknown; tensile strength,[c] 9500 to 11 500 psi (66.5 to 80.5 MN/m^2)					

[a]Tensile strength after 2 cycles, 4000 psi (28 MN/m^2); tensile strength after 4 cycles, 5000 psi (35 MN/m^2).

[b]Too thin to roll beyond 18 cycles.

[c]Current literature value, 14 000 psi (98 MN/m^2).

(a) Ni-3ThO$_2$.

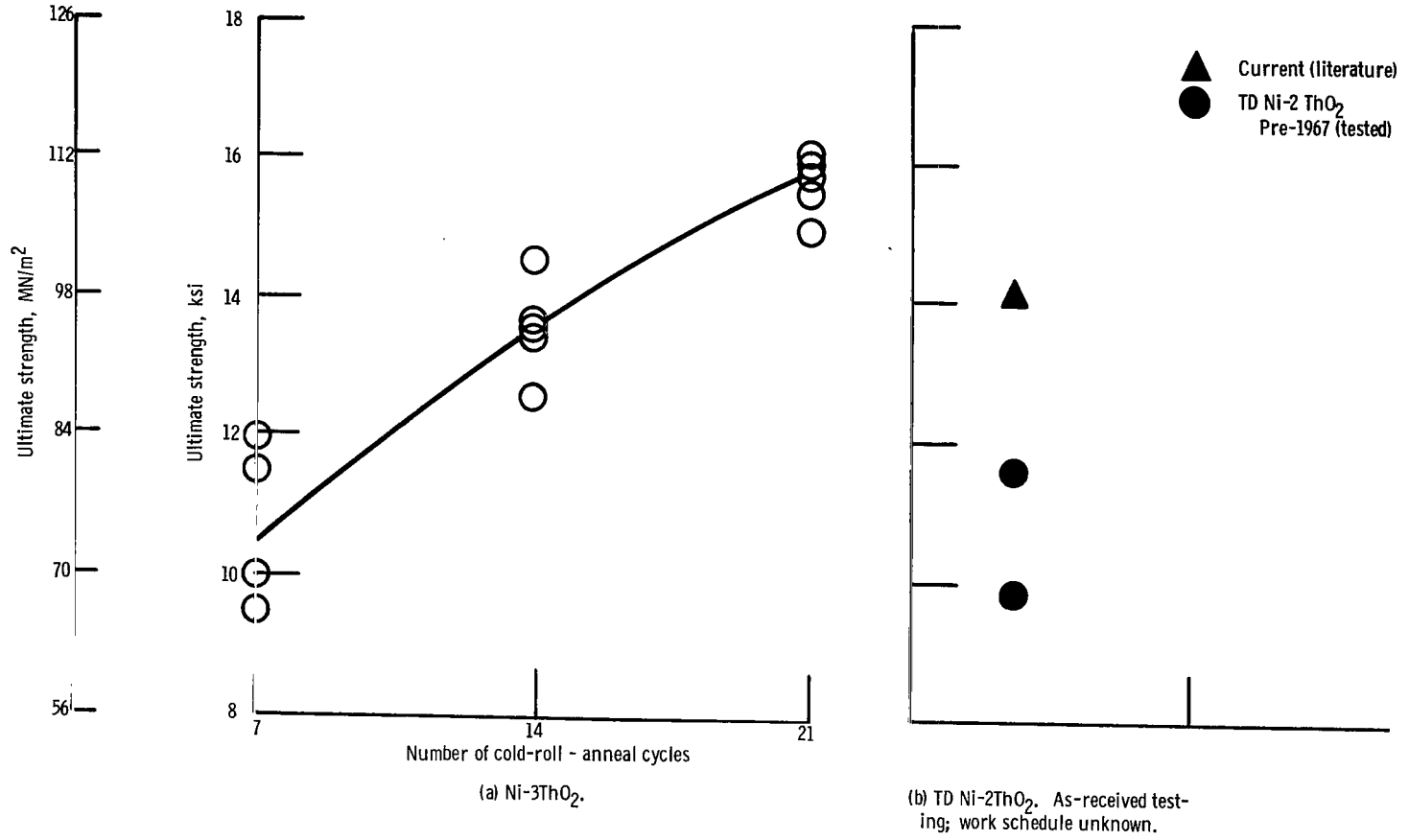(b) TD Ni-2ThO$_2$. As-received testing; work schedule unknown.

Figure 2. - Tensile strength of dispersion-strengthened nickel sheet at 2000° F (1100° C): TD Ni-2ThO$_2$ and Ni-3ThO$_2$ reference sheet.

to values published in reference 2 which were obtained from similar powders by somewhat different processing methods.

Materials Produced by Comminution and Blending

Ni-4ThO$_2$ prepared from Ni and ThO$_2$. - Tensile strengths for the Ni-4ThO$_2$ products prepared by direct grinding of nickel and thoria are shown in figure 3 along with the scatter band for the reference Ni-3ThO$_2$ material. Note that the material given seven cold-roll - anneal cycles was ground in heptane and alcohol. The material given 14 and 21 cycles was ground in heptane plus oleic acid. (Previous studies show little difference
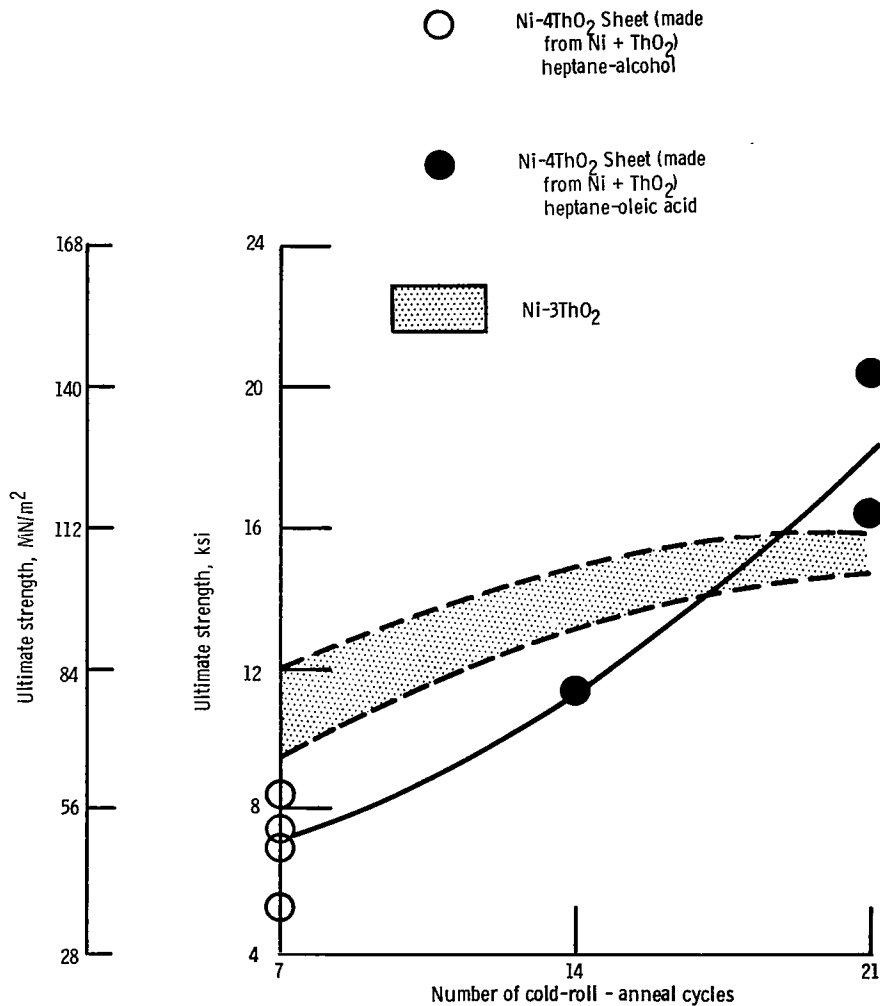
Figure 3. - Tensile strength of dispersion-strengthened nickel sheet at 2000° F (1100° C): NAS-CAB Ni-4ThO$_2$ compared with Ni-3ThO$_2$ reference.

in results between these two media.) There is a general increase in strength with increasing number of cold-roll - anneal cycles. Tensile results range from an average of 7000 psi (49 MN/m^2) for seven passes to 18 500 psi (130 MN/m^2) for 21 passes. The 21-pass material data are above the scatter band of the reference material. Specimen elongations averaged 3.8 percent.

Ni-4ThO$_2$ prepared from NiO + ThO$_2$. - Tensile strengths for the Ni-4ThO$_2$ materials prepared from a selective reduction process of NiO and ThO$_2$ materials ground in heptane-alcohol or water are shown in figures 4 and 5 along with the Ni-3ThO$_2$ reference material. The strongest Ni-4ThO$_2$ material in 2000° F (1100° C) tensile strength was prepared from the NiO plus ThO$_2$ material ground in heptane and alcohol; the maximum tensile strength obtained was 26 000 psi (182 MN/m^2) after 21 cold-roll - anneal cycles. The strength ranged, on an average, from 19 000 psi (133 MN/m^2) in seven cycles to approximately 24 000 psi (168 MN/m^2) after 21 cycles.

The material produced from the water ground product increased appreciably from a very low tensile value of approximately 5000 psi (35 MN/m^2) after seven cycles to
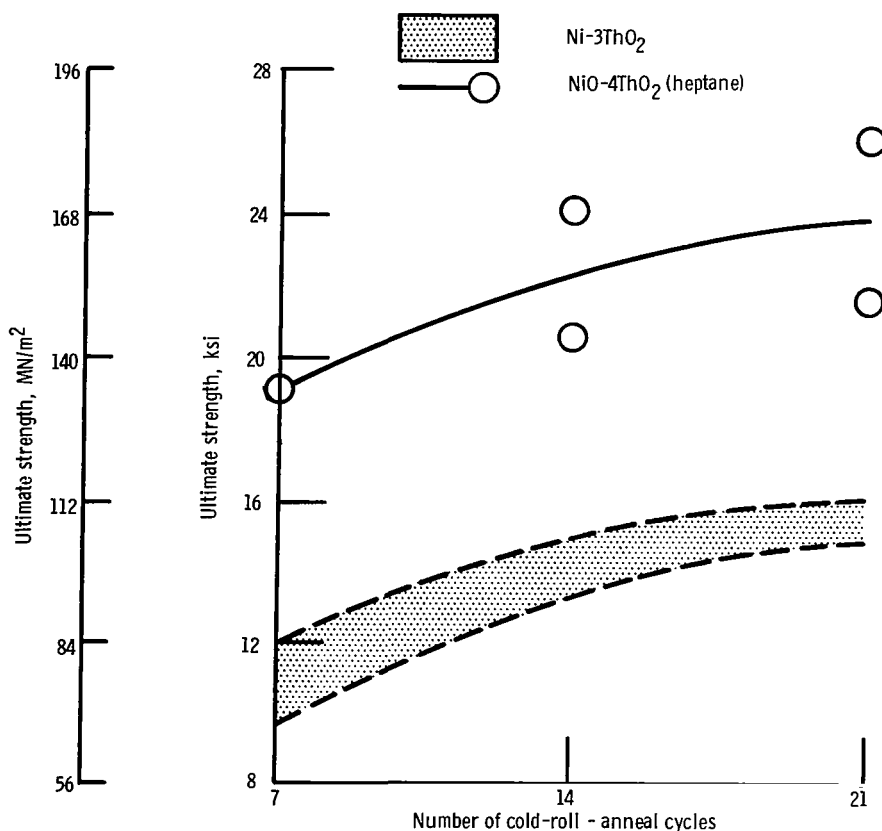

Figure 4. - Tensile strength of dispersion-strengthened nickel sheet at 2000° F (1100° C): NAS-CAB NiO-4ThO$_2$ ground in heptane compared with Ni-3ThO$_2$ reference.
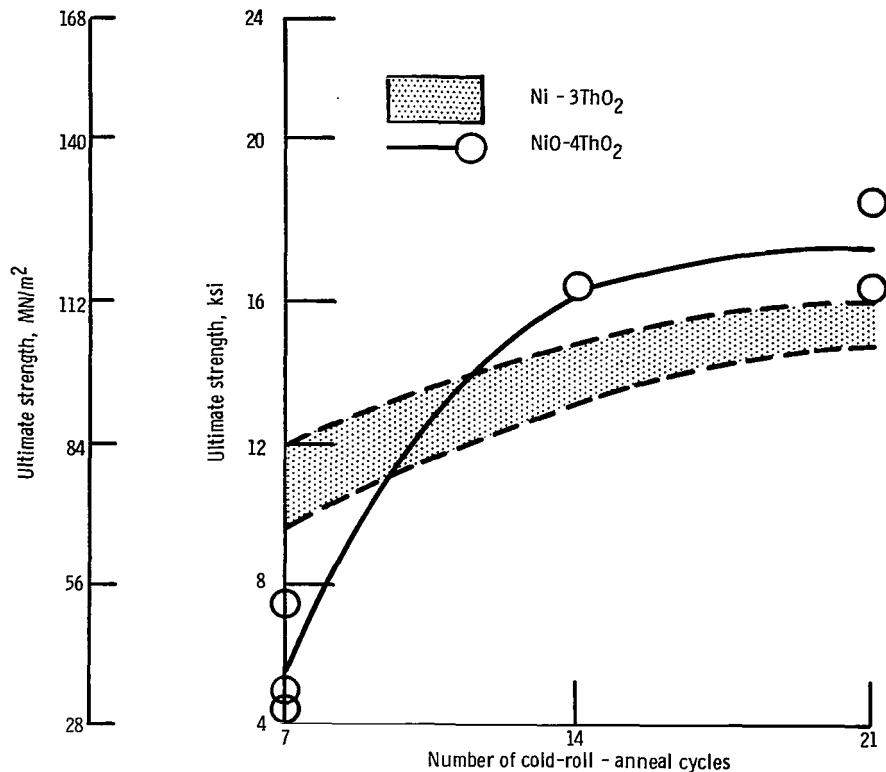
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Figure 5. - Tensile strength of dispersion-strengthened nickel sheet at 2000° F (1100° C): NAS-CAB Ni-4ThO$_2$ from NiO-4ThO$_2$ ground in water compared with Ni-3ThO$_2$ reference.

16 500 psi (115 MN/m^2) after 14 cycles. The increase between 14 and 21 cycles to an average value of 17 500 psi (123 MN/m^2) was relatively slight. The shape of the heptane ground material property curve (fig. 4) almost paralleled the shape of the standard material but at a much higher stress level. Specimen elongations averaged 7.4 percent.

Ni-0.5Zr-4ThO$_2$ prepared from Ni-ZrH$_2$-ThO$_2$. The 2000° F (1100° C) tensile strength results for this material prepared from powders of nickel, zirconium hydride, and thoria are shown in figure 6 along with the properties of the Ni-3ThO$_2$ reference material (scatter band). The peak properties of this NAS-CAB material occurred after seven cold-roll - anneal cycles. Values after seven cycles ranged from 16 500 to 22 500 psi (115 to 158 MN/m^2) an average of approximately 19 000 psi (133 MN/m^2). With increasing number of cycles the strength of this material decreased rather than increased in contrast to the other materials described previously. The Ni-0.5Zr-4ThO$_2$ specimens tested after two and four cycles had low strengths of approximately 4000 to 5000 psi (28 to 35 MN/m^2). This would indicate that the peak strength would be obtained in the vicinity of four to seven cycles. The important thing to note is that the alloying addition of 0.5 percent Zr permitted the achievement of greater strength in the material at fewer
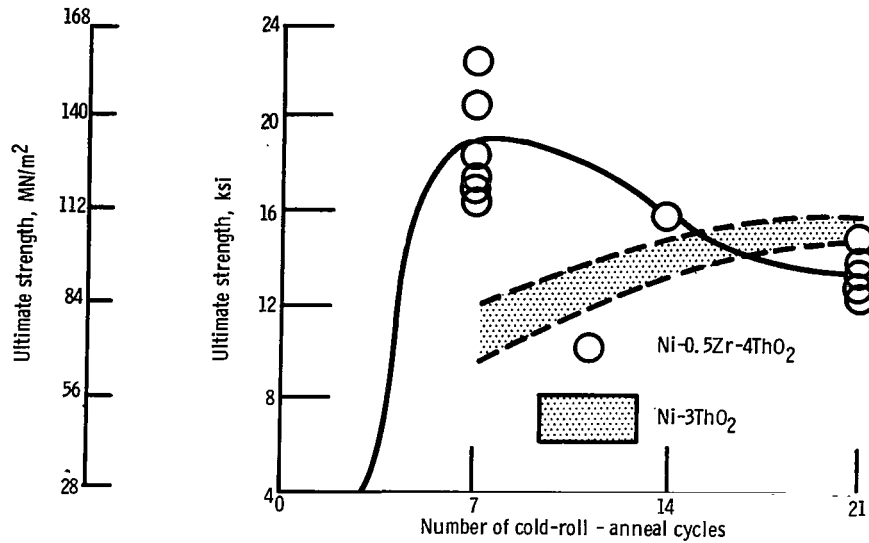
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Figure 6. - Tensile strength of dispersion strengthened nickel sheet at 2000° F (1100° C): NAS-CAB Ni-0.5Zr-4ThO$_2$ compared with Ni-3ThO$_2$ reference.

passes than was observed for the unalloyed nickel matrix with the ThO$_2$. Specimens elongations averaged 4.8 percent.

Ni-2Al$_2$O$_3$. - The 2000° F (1100° C) tensile strength of Ni-2Al$_2$O$_3$ produced by grinding nickel and alumina in heptane are shown in figure 7, again with the comparison of the
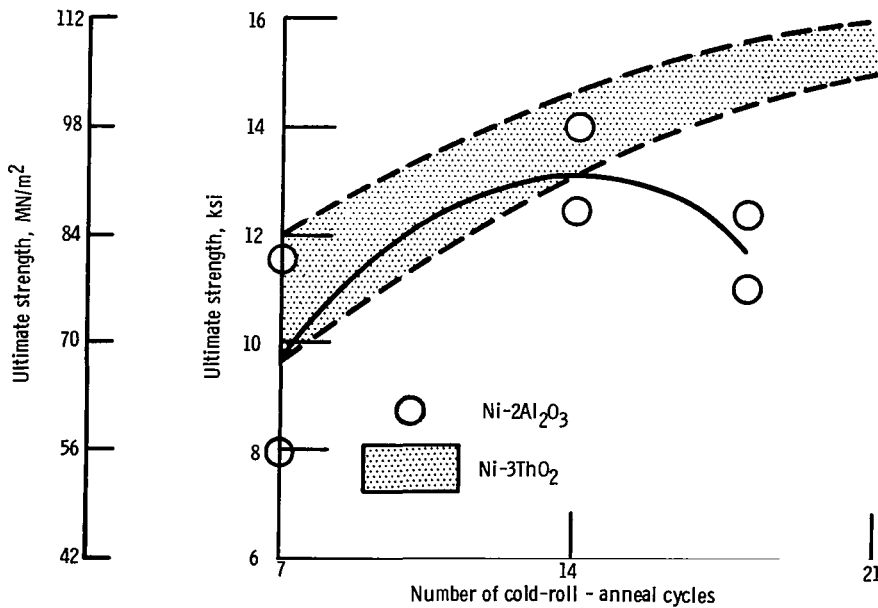

Figure 7. - Tensile strength of dispersion-strengthened nickel sheet at 200 at 2000° F (1100° C): NAS-CAB Ni-2Al$_2$O$_3$ compared with Ni-3ThO$_2$ reference.

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reference Ni-3ThO$_2$ product. Based on limited data, it appears that this material had strengths which peaked after 14 cycles, less strength being obtained at both seven and 18 cycles. (After 18 passes this material was only 5 mils (0.013 cm) thick so the cold roll-anneal cycles were stopped at this point.) At 7 and 14 cycles the tensile strength was comparable to the Ni-3ThO$_2$ but in no case were the properties greater than those of the reference material. Specimen elongations averaged 4.7 percent.

STRESS RUPTURE RESULTS AT 2000° F

Of the materials made at the Lewis only the Ni-0.5Zr-4ThO$_2$ and NiO-4ThO$_2$ heptane products were tested in stress-rupture. The results of these tests are shown in table V and plotted in figure 8. For comparison, figure 8 also includes stress-rupture results for Ni-2ThO$_2$ (TD Ni) procured in sheet form and for the reference material made from the Ni-3ThO$_2$. Some literature data for these reference materials are also included in the figure. Although the data are limited, the points fall close to a straight line extending from stress values for 0.1 hour to rupture to values for rupture times greater than 10 and 100 hours. Similarly, a straight line drawn through all of these points for the com-

TABLE V. - 2000° F (1100° C) STRESS RUPTURE RESULTS

DISPERSION STRENGTHENED NICKEL SHEET

Material	Number of cold-roll - anneal cycles	Stress		Life, hr
		psi	MN/m^2	
NAS-CAB Ni-0.5Zr-4ThO$_2$	7	14.0×10^3	98	5.8 15.4
	7	13.0	91	9.6 14.4
NAS-CAB NiO-4ThO$_2$ (heptane)	7	10.0	70	290
	21			[a]500
Ni-3ThO$_2$	14	10.0	70	5.0
	21			16.5
TD Ni-2ThO$_2$ as-received 0.030 in. (0.08 cm) sheet	--	10.0	70	155
	--	8.0	56	[b]240
	--	7.0	49	[b]450

[a]Extrapolated data.
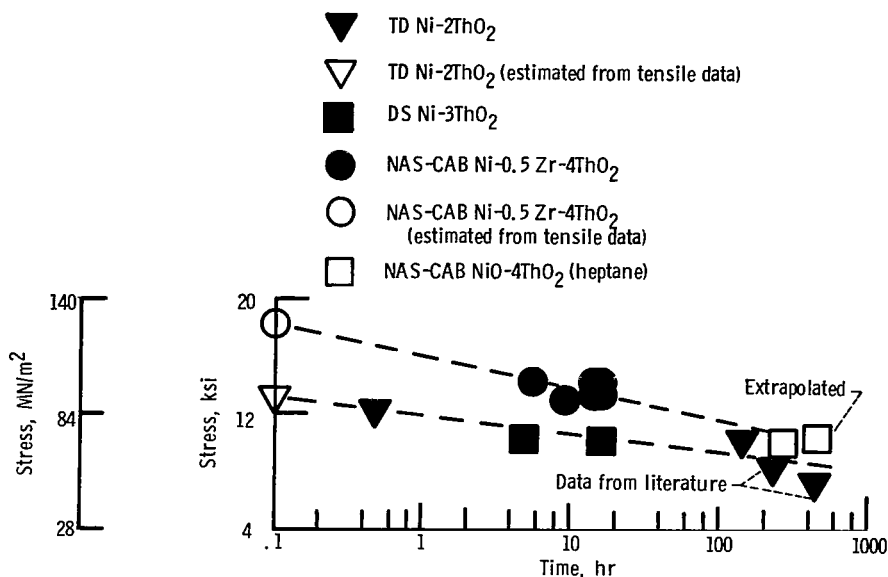[b]Data taken from the literature.

Figure 8. - Stress-rupture properties of dispersion strengthened
nickel sheet at 2000° F (1100° C).

mercial products is believed to represent the relative level of the sheet material produced
either as commercial products or produced by the NASA process applied to chemically
produced commercial powder. Over the entire time range shown, the properties of the
products produced from the comminuted and blended powders are superior to those of the
other products. At 100 hours, for example, there is about a 2000 psi (14 MN/m^2) strength
advantage in the dispersion strengthened material produced in this investigation. At a
stress level of 10 000 psi (70 MN/m^2) there is a time to rupture advantage of approxi-
mately two times (155 versus 290 hr) in the NAS-CAB comminuted and blended product.
This stress rupture test was achieved with a seven-cycle $NiO-4ThO_2$ heptane product
with a 19 000 psi (133 MN/m^2) 2000° F (1100° C) tensile property.

A similar 2000° F (1100° C), 10 000 psi (70 MN/m^2) stress-rupture test of a high
tensile strength (24 000 psi; 168 MN/m^2), 21 cycle $NiO-4ThO_2$ heptane ground product
(interrupted after 211 hr) showed a creep rate of about one-half that exhibited by the best
material described previously. Assuming similar ductilities and elongation, an extrapo-
lated value indicates a stress-rupture life of approximately 500 hours if the test had been
run to failure. While more extensive testing must be done, these data indicate that signif-
icant improvement in stress-rupture properties are achievable with gains in tensile
strength.

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MICROSTRUCTURES

Electron micrographs of selected specimens are shown in figures 9 to 11. These photmicrographs were prepared by conventional replication methods and were taken at an initial magnification of 11 000. At this low magnification it is possible to see larger particles (approx 0.1 to 0.5 μm) which in some cases could be agglomerated oxides or possibly could contain zirconium oxide (inthe Ni-Zr-ThO$_2$) as well as extremely fine particles (<0.05 μm) in the background. No attempt was made to obtain quantitative correlations between strength of materials and microstructures. Some qualitative relations, however, will be pointed out.
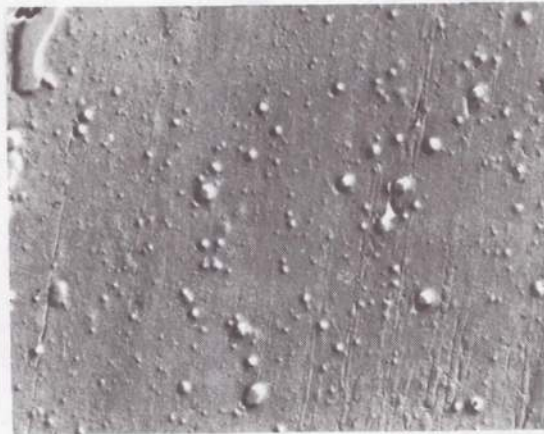
Figure 9 shows a comparison of the reference material, prepared from Sherritt
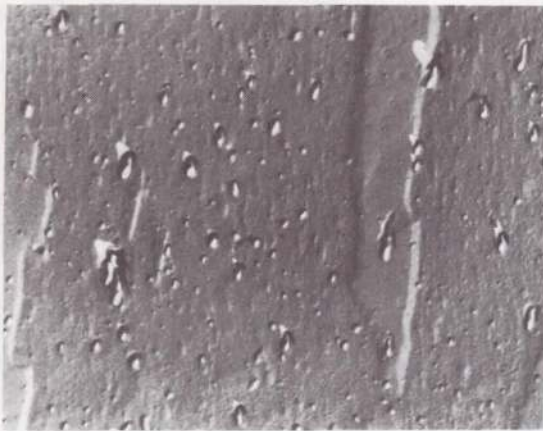
(a) Seven cold-roll - anneal cycles; ultimate tensile strength, 9500 psi (66 MN/m^2).
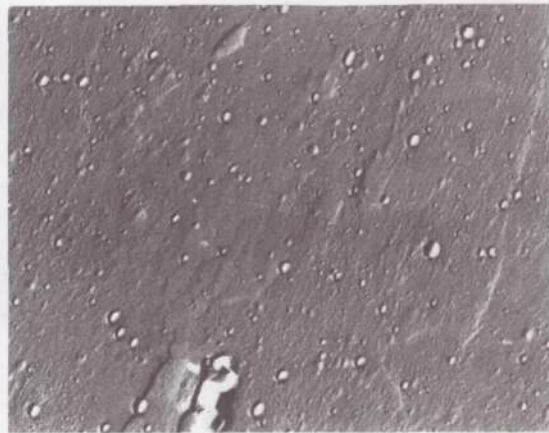
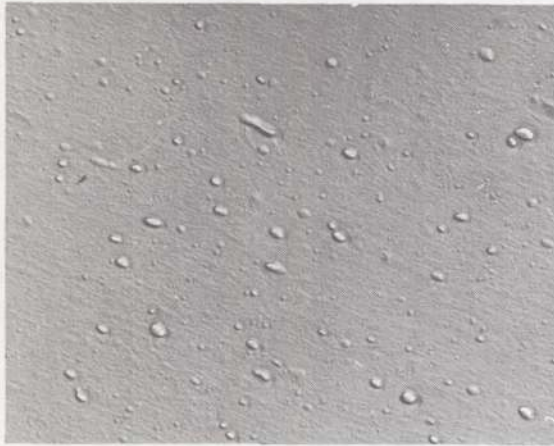(b) Fourteen cold-roll - anneal cycles; ultimate tensile strength, 13 000 psi (95 MN/m^2).

(c) Twenty-one cold-roll - anneal cycles; ultimate tensile strength, 16 000 psi (112 MN/m^2).

Figure 9. - Comparison of microstructures of Ni-3ThO$_2$ made from Sherritt Gordon powder with three different cold-roll - anneal cycles. As-rolled longitudinal structure; tensile tested at 2000° F (1100° C). X11 000.

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Gordon powder, given different numbers of cold rolling-annealing cycles - seven, 14, and 21 cycles. The lowest strength product, produced in seven cycles (fig. 9(a)) appears to have larger particles and fewer extremely fine particles than does the product that was rolled 14 cycles shown in figure 9(b). The microstructure of the strongest (21 cycle) material (fig. 9(c)) is different from the other two, but it is difficult to determine whether there is a higher density of smaller particles in this product. Thin film or extraction micromeasurements of interparticle spacing would be required to make a more significant comparison.

Electron microstructures of the good and poor products prepared by comminution and blending are shown in figure 10. Figure 10(b) is a micrograph of the best product prepared from the $NiO-4ThO_2$ powders ground in heptane. A micrograph of one of the higher strength $Ni-0.5Zr-4ThO_2$ materials (fig. 10(a)) shows some large and many ultrafine particles in the matrix. In figure 10(c) the microstructure of a low strength product

(a) High strength $Ni-0.5Zr-4ThO_2$. Seven cold-roll - anneal cycles; ultimate tensile strength, 22 500 psi (157 MN/m^2).

(b) High strength $NiO-4ThO_2$ (heptane). Twenty-one cold-roll - anneal cycles; ultimate tensile strength, 26 000 psi (182 MN/m^2).
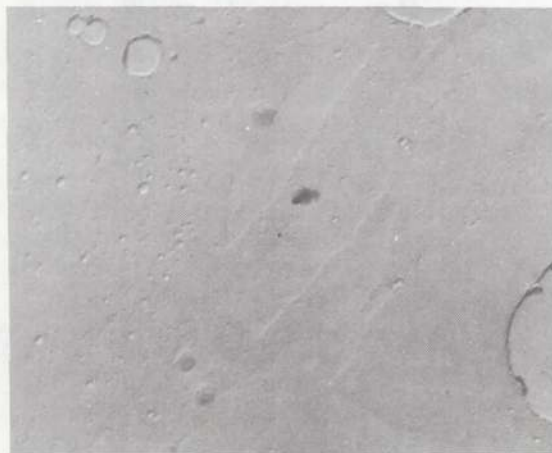
(c) Low strength $Ni-4ThO_2$. Seven cold-roll - anneal cycles; ultimate tensile strength, 7000 psi (49 MN/m^2).

Figure 10. - Comparison of microstructures of high and low strength NAS-CAB materials with varying cold-roll - anneal cycles. Tensile tested at 2000° F (1100° C); longitudinal structures. X11 000.

reveals large areas where there are practically no particles of any type visible. Presumably, these particles agglomerated during the processing.

Figure 11 shows microstructures of Ni-2Al$_2$O$_3$ with varying numbers of cold-roll - anneal cycles. Large particles exist in both microstructures and relatively few small particles can be seen in either material. Presumably they are present but were not revealed by the polish etch procedure employed.

(a) Seven cold-roll - anneal cycles; ultimate tensile strength, 11 500 psi (80 MN/m^2).

(b) Fourteen cold-roll - anneal cycles; ultimate tensile strength, 14 000 psi (98 MN/m^2).

Figure 11. - Comparison of microstructures of Ni-2Al$_2$O$_3$ with varying number of cold-roll - anneal cycles. Tensile tested at 2000° F (1100° C). X11 000.
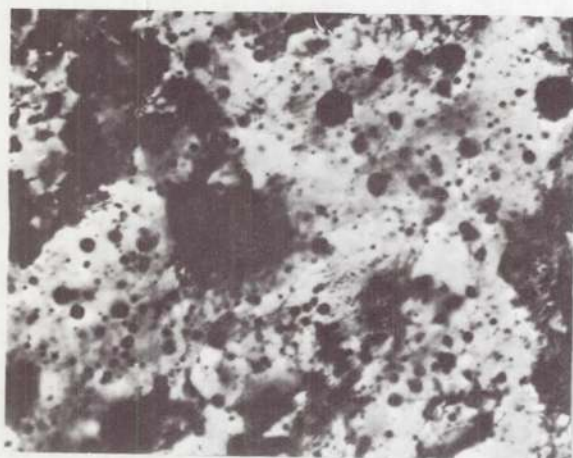
Extraction and thin film electron micrographs of selected specimens are shown in figure 12. Figure 12(a) represents a conventionally replicated Ni-0.5Zr-4ThO$_2$ sample at a magnification of 11 000. The same material is shown in figure 12(b) when given an extraction treatment to remove the dispersoids. The extracted dispersoids embedded in a carbon replica are shown as black dots. A magnification of 46 000 reveals extremely fine particles of oxides. A rough approximation of the interparticle spacing of this material is 0.5 micronmeter. The same material when prepared in a thin film and photographed at 48 000 diameters shows the microstructure noted in figure 12(c). Again, an extremely large number of ultrafine oxide dispersoids are shown in the general background of the material. Figure 12(d) shows the thin film structure of the Ni-3ThO$_2$ reference after seven cycles also at 48 000. It is evident that there are fewer particles in this microstructure per unit of cross-sectional area. Differences in microscopy techniques such as variation in thickness of the thin films could account for some of the differences observed in the strong and weak materials. However, it is believed that the representations shown are real because the general trends noted by conventional replication are verified by extraction as well as thin foil techniques.
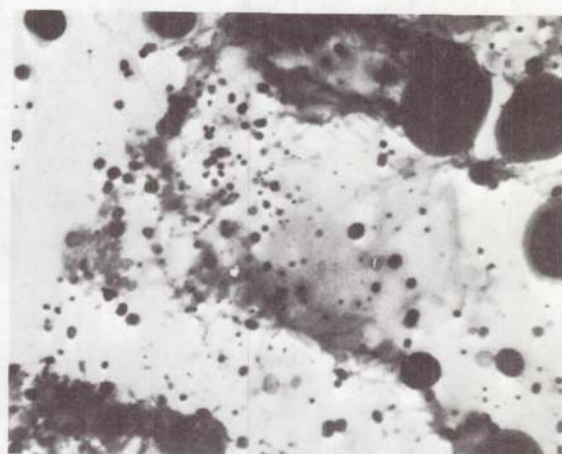
(a) Ni-0.5Zr-4ThO$_2$; replica. X11 000.

(b) Ni-0.5Zr-4ThO$_2$; extraction. X46 000.

(c) Ni-0.5Zr-4ThO$_2$; thin film. X48 000.

(d) Ni-3ThO$_2$ standard; thin film. X48 000.

Figure 12. - Comparison of microstructures of Ni-0.5Zr-4ThO$_2$ and Ni-3ThO$_2$ standard. Seven cold-roll - anneal cycles; replica, extraction, and thin film electronmicrographs.

DISCUSSION OF RESULTS

The results of this investigation have shown not only that high strength dispersion-strengthened products can be produced from mechanically comminuted and blended powders but that strength at temperatures of 2000° F (1100° C) can be varied considerably by variations in thermomechanical processing. Of the several materials produced in this investigation by different methods, two have tensile properties at 2000° F (1100° C) which are 25 percent or more stronger than the best comparable commercial sheet products. One of these products was prepared by grinding NiO and ThO$_2$ together and selectively reducing the NiO to form a product. The second material was produced by grinding metal-

lic nickel with the addition of 0.5 weight percent zirconium in the form of a hydride plus 4 volume percent ThO_2. These materials were tested in stress rupture and compared with the rupture results of comparable commercial sheet material products. In these cases the stress carrying capacity for a 100-hour life was about 20 percent superior to commercial sheet products or on the basis of life for a constant stress level of 10 000 psi (70 MN/m^2), failure times were approximately two to three times greater. Until this point the only dispersion-strengthened products which had been made to have good high temperature properties at 2000° F (1100° C) were produced by chemical or chemical-colloidal approaches. Now it appears that with the versatile mechanical approach more dispersoid or alloy additions may be incorporated into materials or the process can be applied directly to alloys offering a possibility for greatly improved strengths.

Effects of Thermomechanical Working on Tensile Properties

It has long been known that the properties of metals and alloys can be improved by thermomechanical processing. Two aspects are of particular interest in the case of dispersion-strengthened materials. One is that the presence of finely dispersed stable particles can assist in retaining at high temperatures some of the strain energy introduced by thermomechanical processing. The second is that by sequential working with small reductions and annealing between reductions, high temperature strength improvement can be achieved (refs. 2 and 9). In the working performed during this investigation the initial hot reductions are done to achieve a fully dense product. The mechanism of strengthening suggested in reference 2 is that, during the cold rolling portion of the thermomechanical processing, a dense dislocation network is produced. On annealing, the dislocations are swept into low angle subgrain boundaries which are pinned in position by the fine particles. Experiments noted in reference 2 show that much better properties are obtained with low 5 or 10 percent rolling passes as opposed to higher reductions.

The general trend of increasing the 2000° F (1100° C) tensile properties with increasing numbers of cold-roll - anneal cycles was observed for the specimens made from Ni-4ThO$_2$, from NiO-4ThO$_2$, Ni-2Al$_2$O$_3$, and the Ni-3ThO$_2$ reference material. Of these materials the best properties obtained were those produced from a NiO-4ThO$_2$ blend by the selective reduction of NiO to Ni with the ThO$_2$ remaining unchanged. Figure 3, which shows the properties of this material, indicates that the best properties of 26 000 psi (182 MN/m^2) were obtained after 21 cold roll-annealing cycles, a considerable rise from the properties obtained after seven cold roll annealing cycles. The material that had the second best properties was the Ni-0.5Zr-4ThO$_2$. Here a converse situation was observed, namely, the best properties obtained occurred after seven cold-roll - anneal cycles and with increasing numbers of cycles the properties decreased significantly. This suggests that the alloying addition caused the response of the material to be completely

different from that of the unalloyed matrix material. As such, a material like this would be more economical to fabricate to a given strength in that fewer reductions or passes to achieve strength would be necessary to optimize the properties. It is possible that the small percent of alloying element perhaps could also permit a material to achieve its s strength by working practices other than rolling.

Zirconium was added initially to act as a scavenger in removing the remaining impurities that might not have been removed by the cleaning process. In addition, it was felt that the zirconium would increase the adhesion between the matrix and the particle. Presumably, there would be a residue of zirconium in the matrix which could strengthen the matrix which could strengthen the matrix somewhat by solid solution strengthening, and enhance the work hardening rate of the material. Clarifying the actual condition of the zirconium in the alloy would be possible from X-ray and electron diffraction and by chemical analysis. This was not done as part of this investigation.

Stress Rupture

All but two of the stress-rupture specimens tested were the Ni-0.5Zr-4ThO$_2$ alloy, the others being NiO-4ThO$_2$ ground in heptane. The tensile strengths of the Ni-0.5Zr-4ThO$_2$ material were on an average as high as 19 000 psi (133 MN/m^2) after seven cold-roll - anneal cycles. The stress- rupture test of the material, which had tensile values as high as 26 000 psi (182 MN/m^2) without the zirconium, was also run at a stress of 10 000 psi (70 MN/m^2). Although this test was interrupted after 211 hours, the creep rate indicated that the stress-rupture properties should be considerably above that of the Ni-0.5Zr-4ThO$_2$ alloy. With both NASA compositions, the rupture values were considerably better than those of the reference materials.

These results are of particular significance because while relatively rapid, easy to perform tensile tests were being used to screen the good materials produced in the investigation, the true value of dispersion-strengthened products are in long time high temperature applications. Thus tensile tests are a relatively valid screening test for this type of material. Substantial gains in stress-rupture properties accompanied increased tensile strengths.

Microstructures

The microstructures vary considerably from material to material. Although no quantitative measurements of the given structures were made, qualitative measurements indicated that the materials with better properties did have a finer dispersion of ultrafine

particles throughout the structure. Many structures, both those with zirconium and without, had fairly large particles within the material. These may have been agglommerates that occurred during the processing or in the case of the zirconium bearing material, zirconium could be present in the larger particles as well. If these large particles could be eliminated, it is possible that the materials could be even stronger.

Significance of Volume Percent of Dispersoid Oxide

Throughout the text of this investigation several comparisons have been made to different products produced by others. One had 3 weight percent and the other 2 volume percent of oxide dispersoids. It could be argued that by the simple expedient of increasing the oxide content the properties of the product produced herein would increase, and this may be true. There are, on the other hand, many reasons why this type of relation does not necessarily hold. Because the subject is relatively complex, only a few points will be made which are pertinent to the current investigation. In general, increasing the oxide content should decrease the interparticle spacing and increase the strength of dispersion products, but other factors, such as composition and powder processing variables, oxide agglomeration, type of working, and thermomechanical processing schedule employed, actually determine how far properties can be improved with increased oxide concentration. This is indicated by the data of reference 2, which shows a maximum strength obtained at 3 to 3.5 weight percent ThO_2. While no optimum maximum oxide concentration level was determined with the NASA method, it is significant that good properties were achieved with both 2 and 4 percent oxide products.

The point was made earlier that the thermomechanical working process produced a fine substructure, which was stabilized by the dispersoids. The particle sizes of the dispersoids (which have been examined) along with the volume percent determine the interparticle spacing, which is of importance in influencing the thermomechanical working process. It is beyond the scope of this paper, however, to examine and correlate the different variables and parameters, particularly particle spacing and working with the production of fine grain size and substructure.

CONCLUSIONS AND SUMMARY OF RESULTS

This investigation was conducted to determine whether dispersion-strengthened materials with properties comparable to those of the best nickel base commercial materials could be made from comminuted and blended products. The effect of thermomechanically working such materials to varying degrees was also studied. The following results were

obtained with various compositions annealed and cold rolled seven, 14, or 21 times after hot rolling.

1. Dispersion strengthened nickel base materials with 2000° F (1100° C) tensile properties and stress-rupture properties equal to or better than comparable commercially produced dispersion-strengthened nickel base sheet materials were prepared by comminution, blending, sintering, and thermomehcanical working processes.

2. The best 2000° F (1100° C) tensile properties were obtained with a nickel oxide - 4-volume percent thoria ($NiO-4ThO_2$) composite powder ground in heptane alcohol and selectively reduced to produce a nickel - 4 volume percent thoria ($Ni-4ThO_2$) dispersion-strengthened product. The best 2000° F (1100° C) tensile property obtained in this case was 26 000 psi (182 MN/m^2) after 21 cold roll-anneal cycles. Maximum 2000° F (1100° C) tensile strength obtained by similar processing but from a reference nickel - 3 weight percent thoria ($Ni-3ThO_2$) powder was 16 000 psi (112 MN/m^2).

3. The next best 2000° F (1100° C) tensile strengths ranged up to 22 500 psi (157 MN/m^2) with an average of 19 000 psi (133 MN/m^2) and were achieved with a nickel - 0.5 volume percent zirconium - 4 volume percent thoria ($Ni-0.5Zr-4ThO_2$) composition. The material was given only seven cold-roll - anneal cycles. Addition of the zirconium changed the response of the cold-roll - anneal cycles and a stronger product was produced with less thermomechanical processing cycles.

4. In general, the strength properties increased with increasing amounts of thermo-mechanical processing up to 21 cold roll-anneal cycles. This was noted with the $Ni-4ThO_2$ and $NiO-4ThO_2$ compositions as well as the reference $Ni-3ThO_2$. With $Ni-0.5Zr-4ThO_2$ a peak tensile strength was noted after seven cycles and the strength decreased with additional roll-anneal cycles. Nickel - 2 volume percent aluminum oxide increased in strength to the 14 cycle level and then decreased in strength with further cold-roll - anneal cycles.

5. A limited number of tests show the 2000° F (1100° C) stress-rupture properties of the comminuted and blended $Ni-0.5Zr-4ThO_2$ and $Ni-4ThO_2$ (made from $NiO-4ThO_s$ ground in heptane) sheet materials to be superior to those of the $Ni-3ThO_2$ reference material. An interrupted stress-rupture test (discontinued because of equipment failure) of a sheet material produced from a selectively reduced $NiO-4ThO_2$ heptane grind with 21 working cycles ran 211 hours with a 10 000 psi (70 MN/m^2) load. The specimen had a much lower creep rate than the $Ni-0.5Zr-4ThO_2$ product. Extrapolation indicated that failure would have occurred at 500 hours.

6. Small changes in matrix composition and changes in powder processing appear to influence the response of the dispersion products to thermomechanical working. More study of such variables appears to be warranted.

7. Electron micrographs of conventionally replicated comminuted and blended dispersion strengthened products contained finer particles than did a reference product.

Along with fine particles ($<0.05\mu m$), numerous large particles of the order of 0.1 to 0.5micrometers were also present. Extraction and thin foil microscopy studies corroborated the replication studies and revealed that a high density of ultrafine dispersoids existed in comminuted and blended products examined. Fine particle sizes, coupled with fine interparticle spacing of dispersoids are believed to account in part for the strength of these products. It is felt that better products may be achieved if processing were optimized to produce still finer more uniform dispersions.

Lewis Research Center,
 National Aeronautics and Space Administration,
 Cleveland, Ohio, July 24, 1969,
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