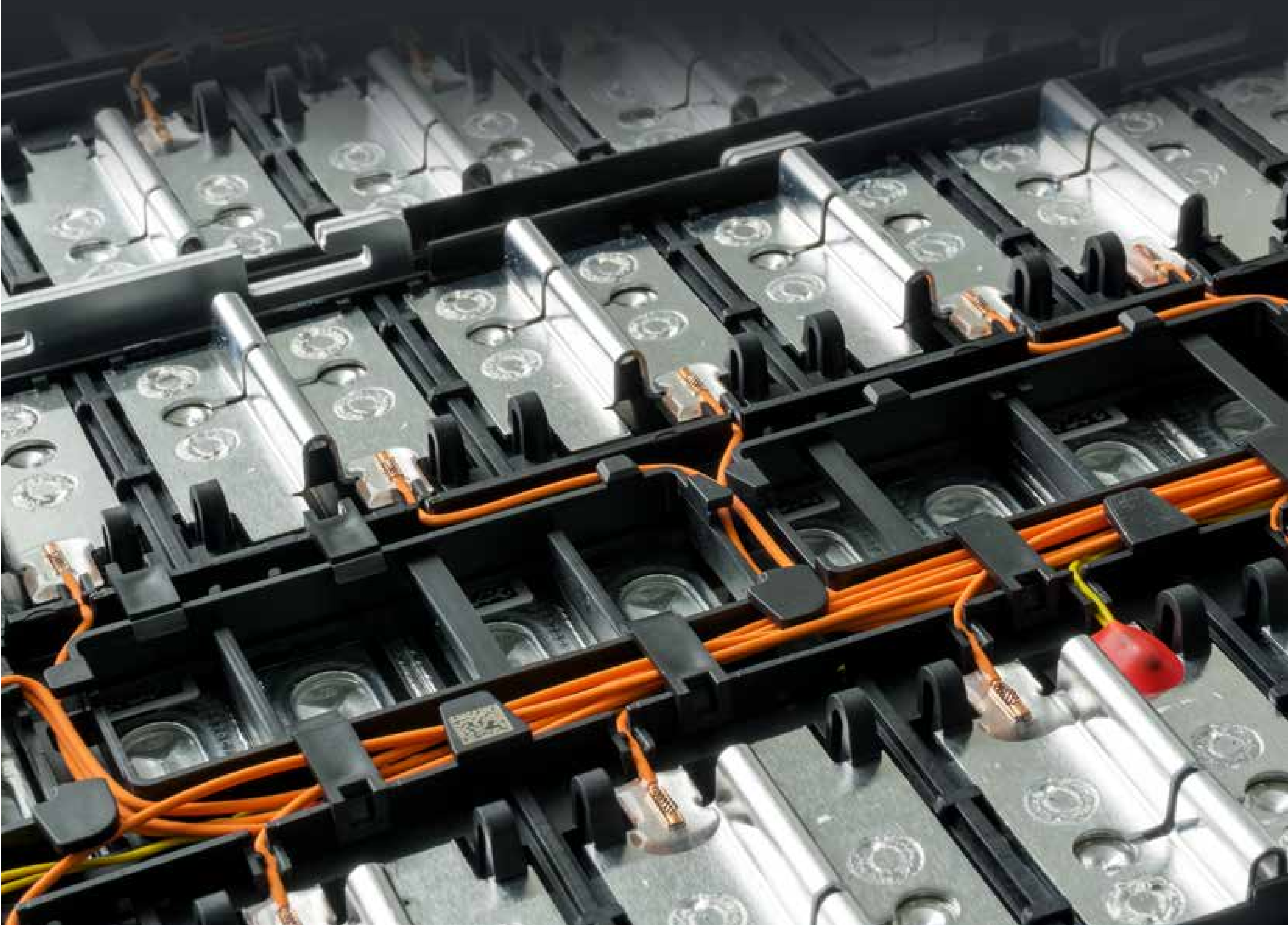
AMETEK®
SPECIALTY METAL PRODUCTS
WALLINGFORD

HIGH PURITY NICKEL STRIP

THE BENEFITS OF COMMERCIALLY PURE WROUGHT POWDER METALLURGY ALLOY STRIP IN BATTERY SYSTEMS.



ABSTRACT

Described herein are high purity wrought powder metallurgy alloys which conform to the general compositional description of commercially pure nickel (99% min. Ni+Co) yet offer property advantages for battery applications which are not available in conventional cast and wrought commercially pure alloy grades.

In particular, the powder metallurgy approach enables use of very low level alloy additions with favorable impact on mechanical, welding, and other properties without detracting from the high electrical and thermal conductivity achievable for high purity materials. Application details requiring special properties are noted and property comparisons are given between powder metallurgy and melted materials.

INTRODUCTION

Commercially pure nickels have been available for many years. They are used in a variety of applications because of a unique combination of properties such as good electrical and thermal conductivity, resistance to tarnishing or chemical reactivity in ambient temperature, atmospheric environments, good formability, ease of plating, good weldability, moderate resistance to acids and excellent resistance to caustic solutions.

Metallurgically, the alloys may be described as single-phase, face-centered, cubic-solid solution alloys. Phase stability and general low chemical reactivity impart a practically useful degree of metallurgical simplicity. The alloys are thus easy to work with in many processing steps.

Exceptions to the above general comments on metallurgical simplicity do exist. The alloys are sensitive to sulfur pick-up and can be embrittled by sulfur. Carbon embrittlement is also possible during long-term exposures at 600^{0}F and above if carbon exceeds about 0.02 weight percent. The high purity nature of the alloys also results in significant property changes on a percentage basis for small variations in impurity and/or alloying levels and can result in excessive grain growth during component fabrication or assembly thermal treatments.

Described herein are powder metallurgy alloys resulting from over 40 years of experience in powder metallurgy process and alloy developments. Alloys with tailored properties have been developed which circumvent problems that can be encountered with high purity nickel. Alloys featuring these tailored properties have already found applications in a range of energy systems including a 10,000 ampere-hour lithium-thionyl-chloride cell, lithium-iodine cardiac pacemaker cell, and conventional AA and D nickel-cadmium cells.

With the properties described herein, designers of future systems can rely on state-of-the art high purity powder metallurgy strip alloys to perform in high reliability applications in the most demanding environments.

POWDER METALLURGY STRIP PROCESS OVERVIEW

Specific details of the AMETEK Specialty Metal Products alloying and processing powder metallurgy technology for nickel strip are proprietary and thus will not be elaborated upon. General steps are **(a)** preparation of elemental blends from carbonyl nickel powder containing less than 20 ppm metallic impurities, **(b)** roll compaction of powder into strip having a thickness of approximately 0.125 inch, **(c)** sintering, and **(d)** further densification, homogenization, and purification of the strip using a series of cold roll and thermal treatment steps. Material is exposed to a temperature of 22000F or above. Roll compaction and sintering steps are continuous. All rolling is performed cold and thus hot working alloying additions are not required. The majority of applications involve strip thicknesses that have been reduced 50% and more by cold rolling. The term, "wrought powder metallurgy strip" is sometimes used to differentiate the product from other powder metallurgy products which have been compacted and sintered but not worked to full density to optimize mechanical properties.

ALLOY DESIGNATIONS AND CHEMISTRIES

Four common commercially pure alloy grade types are shown in Table 1. Included are selected compositional notes for each grade.
Table 2 shows other compositional specifications for AMETEK SMP grades.

Table 1. Alloy Designations:
Selected Commercially Pure Nickels (99% Min. Ni+CO)

UNS Number	Compositional Notes	AMETEK Alloy Grades
N02270	99.97% min. Ni	AME270-899A
N02233	0.01 - 0.10/0 mg	AME205-899D
N02201	0.02% C max.	AME200-899L AME201-899M
		AME205-899D AME205-899E
N02200	0.15% C max.	AME200-899L AME201-899M
		AME205-899D AME205-899E

The alloy grades listed left are available in these size ranges:

Thickness: 0.001" (0.05mm) to 0.100" (2.54mm)

Width: 0.060" (1.52mm) to 13.50" (345mm)

Vickers Hardness Range: (Dead Soft to Full Hard) 64-210

Coil Sizes offered: (Inside diameter): 3" (76mm), 6" (152mm), 8" (203mm), 12" (203mm), 16" (405mm)

Coil Sizes offered: (Outside diameter): 36" (915mm max)

Table 2. Chemical Composition in Percent

ALL VALUES ARE MAXIMUM WEIGHT PERCENT UNLESS INDICATED AS TYPICAL

ALLOY AME270-899A		UNS Equivalent ALLOY N02270		ALLOY AME200-899L		UNS Equivalent ALLOY N02201, N02200	
C	0.02	C	0.02	C	0.02	C	0.15
Co	0.001	Si	0.001	Co	0.01	Co	0.35
Cr	0.001	Mn	0.001	Cr	0.005	Mn	0.35
Si	0.001	S	0.001	Si	0.005	S	0.01
Mn	0.001	Cu	0.001	Mn	0.05 typical	Cu	0.25
S	0.0005	Fe	0.0005	S	0.001	Fe	0.40
Cn	0.001	Mg	0.001	Cn	0.005	Mg	-
Fe	0.005	Ti	0.005	Fe	0.05	Ti	-
Mg	0.001	Co	0.001	Mg	0.002	Co	-
Sn	0.001	Cr	0.001	Sn	0.005	Cr	-
Al	0.001	Ni	99.97 MIN	Al	0.005	Ni	99.0 MIN
Ti	0.001	-	-	Ti	0.005	-	-

ALLOY AME201-899M		UNS Equivalent ALLOY N02201, N02200		ALLOY AME205-899D		UNS Equivalent ALLOY N02201	
C	0.02	C	0.15	C	0.02	C	0.15
Co	0.01	Si	0.35	Co	0.01	Co	0.35
Cr	0.005	Mn	0.35	Cr	0.005	Mn	0.35
Si	0.005	S	0.01	Si	0.005	S	0.01
Mn	0.02 typical	Cu	0.25	Mn	0.03 typical	Cu	0.25
S	0.001	Fe	0.40	S	0.001	Fe	0.40
Cn	0.005	Mg	-	Cn	0.005	Mg	-
Fe	0.05	Ti	-	Fe	0.05	Ti	-
Mg	0.002	Co	-	Mg	0.015 typical	Co	-
Sn	0.005	Cr	-	Sn	0.005	Cr	-
Al	0.005	Ni	99.0 MIN	Al	0.005	Ni	99.97 MIN
Ti	0.005	-	-	Ti	0.005	-	-

Table 2. Chemical Composition in Percent

ALL VALUES ARE MAXIMUM WEIGHT PERCENT UNLESS INDICATED AS TYPICAL							
ALLOY AME225-899G		UNS Equivalent ALLOY N02233		ALLOY AME205-899E		UNS Equivalent ALLOY N02233	
C	0.02	C	0.15	C	0.02	C	0.15
Co	0.01	Si	0.10	Co	0.01	Co	0.10
Cr	0.005	Mn	0.30	Cr	0.005	Mn	0.30
Si	0.005	S	0.008	Si	0.005	S	0.008
Mn	0.03 typical	Cu	0.10	Mn	0.20 typical	Cu	0.10
S	0.001	Fe	0.10	S	0.001	Fe	0.10
Cn	0.005	Mg	0.01 - 0.10	Cn	0.005	Mg	0.01 - 0.10
Fe	0.05	Ti	0.005	Fe	0.05	Ti	0.005
Mg	0.012 typical	Co	-	Mg	0.001	Co	-
Sn	0.005	Cr	-	Sn	0.06 typical	Cr	-
Al	0.005	Ni	99.0 MIN	Al	0.005	Ni	99.0 MIN
Ti	0.005	-	-	Ti	0.005	-	-

UNS N02201has the same chemistry requirements as N02200 except C is 0.02% maximum.

WELDABILITY

Welding methods frequently used in component assembly are resistance spot welding, gas tungsten arc welding (GTAW), and laser welding. Important alloy parameters for making high reliability GTAW and laser welds are low gas content, low inclusion levels and addition of a strong to moderate oxide former for scavenging of oxygen. Use of a cover gas having oxygen gettering potential significantly improves weld integrity.

A cover gas of high purity argon with 3% hydrogen (30 ppm H_20 maximum) is recommended. In laser welding, use of a straight argon cover gas without hydrogen will result in significantly higher levels of voids and oxide stringers. The same tendencies are observable in GTAW. These weld defects are unacceptable potential leak sites in casing header welds in high reliability lithium-thoinyl-chloride batteries.

Grade AME270-899A is recommended only for resistance spot welding as the alloy is prone to gas void formation in high speed, 40 inch/minute and above GTAW and laser welding. Approved AMETEK SMP welding grades are AME200-899L and AME205-889D and typical welding grade chemistries are noted in Table 3. Welds in these alloys are typically very clean with respect to oxide stringers and impunity element segregation at current grain. Generic Unified Number System (UNS) numbers, and AMETEK SMP alloy grades supplied to the generic UNS alloy type. Alloy N02270 has always been produced via a powder metallurgy approach as the specified high purity level does not permit additions required in melting for proper melt deoxidation and adequate ingot hot-workability. Alloy N02201 has historically been the most widely used of the alloys shown. Alloy N02233 is seldom specified for battery applications.

Table 2 provides additional compositional details for AMETEK SMP grades and those elements which are included as maximums for N02200 and N0220l. Silicon, manganese, copper, sulfur, and iron maximums are much lower in AMETEK SMP grades than the N0220l specification, and as will be evident from property comparisons shown later, are also lower than typical currently produced melted alloy chemistries.

Standard alloying elements used in AMETEK SMP alloys are manganese, magnesium and tin. Magnesium is combined as a fine MgO dispersed phase and as noted in Table 2 the magnesium containing AME205-899D, AME205-899E and AME205-899G grades are noted as "dispersed phase" alloys. Alloying addition levels are closely controlled at plus or minus l00 ppm (by weight) on magnesium and tin and at levels of plus or minus 100-500 ppm on manganese with the actual manganese range depending upon alloy type. These very tight controls on alloying ingredients coupled with the very high purity of the carbonyl-nickel powder are the basis for the unusual chemical reproducibility and attendant property control for the alloys.

Table 3. Typical AME200-899L and AME205-899D Welding Grade Chemistries

	Grade - Typical Level, PPM	
Element	**AME200-899L**	**AME205-899D**
Mn	500	2000
O	30	100[1]
C	200	200
N	1-2	1-2
H	1-2	1-2

[1] *80 PPM combined as MgO*

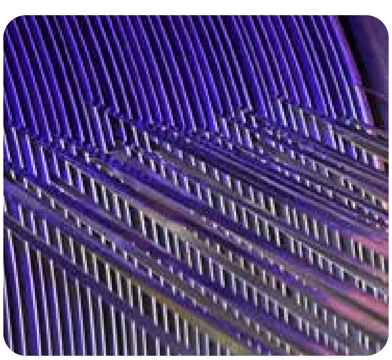
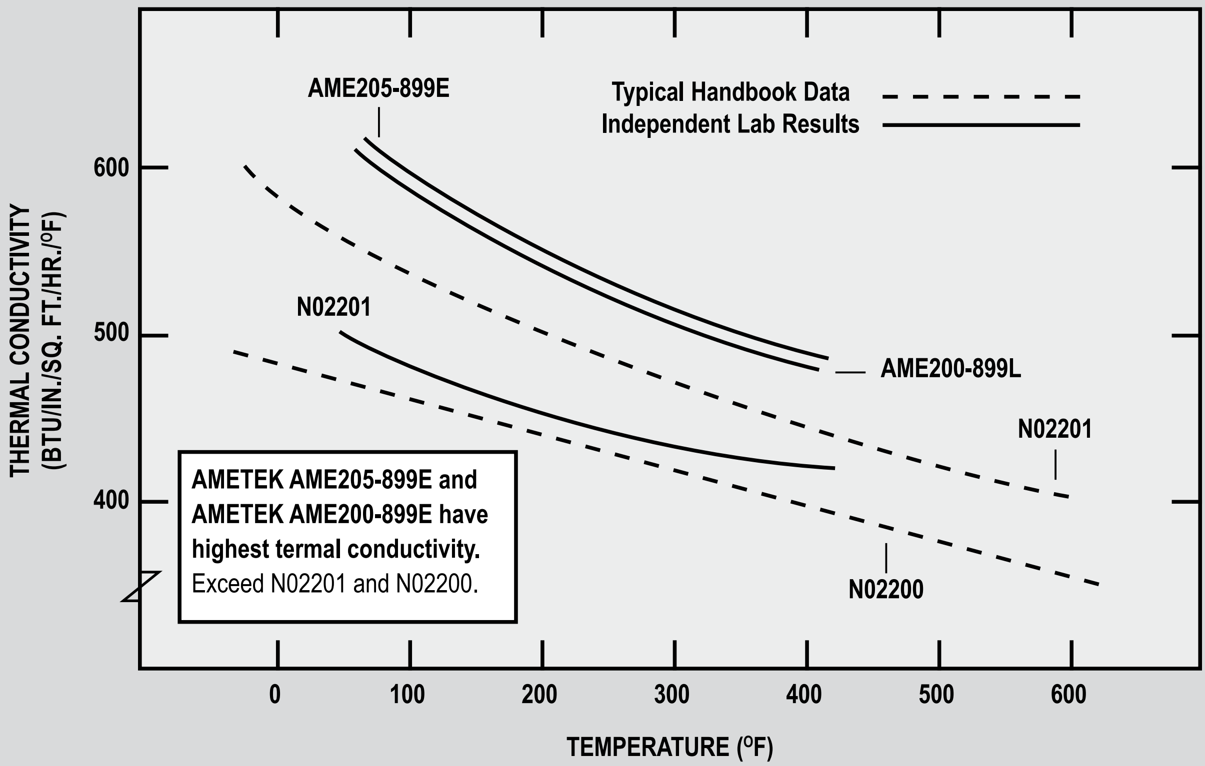


FIGURE 1. THERMAL CONDUCTIVITY



THERMAL CONDUCTIVITY

Thermal conductivity versus temperature is shown in Figure1. Comparison of independent laboratory results indicates approximately 10% higher thermal conductivity of AME200-899L over N02201. The combination of higher thermal conductivity and lower electrical resistivity combine to reduce temperature excursions during overload conditions.

PROPERTIES

Selected nickel properties of importance to system designers and component fabricators are presented. In tables or graphs showing comparative properties for AMETEK SMP and competitively produced melted product, UNS numbers are used for melted alloys and AME200-899 grade letter descriptions for AMETEK SMP alloys.

Unless noted otherwise, competitive values were determined on commercially obtained samples tested in AMETEK SMP laboratories. Emphasis is given AME200-899L and AME205-899D grades in the property discussions as these grades offer specialized properties for battery applications.

Table 4. Electrical Resistivity at 70° F for AME200-899 Nickel *OHM/CMF*

NICKEL GRADE	ANNEALED	50% COLD WORK
AME270-899A	44.5	45.0
AME200-899L	45.1 (c)	45.6
AME201-899M	46.7	47.6
AME205-899D	47.3	47.8
AME205-899E	48.1	48.6
AME205-899G	45.0	45.5
COMPARATIVE DATA FOR WROUGHT AND CAST NICKEL		
UNS N02270	45.0 (a)	
UNS N02201	59.6	62.2
UNS N02201	52.0 (b)	
UNS N02200	57.0	59.2

(a) Wrought powder metallurgy (b) Handbook value (c) Special grade with 44 maximum value available

ELECTRICAL RESISTIVITY

Values are shown in Table 4 for annealed and 50% cold-worked tempers. The low values for AME270-899A explain usage as a tab material in special military applications requiring lowest available electrical resistivity in a commercial nickel. However, grade AME200-899L is recommended herein for general usage in components requiring low electrical resistivity as electrical resistivity is only slightly higher (1.3%) and the alloy offers resistance to sulfur embrittlement, improved formability, and much better weldabllity.

In the annealed condition, AME200-899L offers an 18.9% resistivity advantage compared with a mean value of 55.6 ohm/cmf for the four melted heats. Reproducibility is an additional expected typical advantage as the PM approach routinely achieves resistivity variations within plus or minus 2%. A plus or minus 7.2% variation applies to the 55.6 ohm/cmf mean value for the melted heats. These cited annealed advantages are actually somewhat greater for cold-worked tempers.

Shown in Figure 2 is a microstructure of a CO_2 laser edge weld with AME205-899D alloy. Boundaries in material are adjacent to the heat affected zone (HAZ). Weld parameters were continuous wave mode, 900 watts, and 60 inches/minute with an Ar-3% H_2 cover gas. Penetration approximates 0.030 in. Similar laser welding parameters are used in AME200-899L cathode - bus bar and anode - bus bar weldments in a 10,000 ampere - hour lithium thionyl chloride battery.

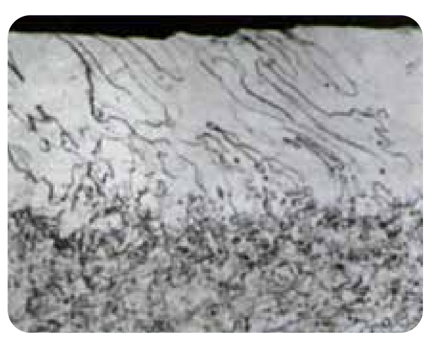


Figure 2. *Longitudinal Section of CO_2 Laser Edge Weld in AME205-899 Alloy, 50X.*

GRAIN GROWTH

Excessive grain growth can be encountered in high purity nickel during component processing and/or assembly steps. Examples are annealing of drawn parts and the preparation of nickel-to-ceramic joins using copper as a brazing alloy material. Development of large grains reduce mechanical strength and may reduce resistance to chemical attack in aggressive environments. As noted in the following, dispersed phase AMETEK SMP grades conveniently prevent grain growth problems.

Comparative grain growth behaviours for a 50% cold-worked condition are noted in Table 5 for several AMETEK SMP and melted grades. Grain sizes are represented by ASTM numbers which decrease as grain size increases. The largest and smallest sizes are 180 microns and 11 microns for ASTM numbers 2 and I0, respectively. With the exception of AME270-899A other AME200-899 grades clearly exhibit greater resistance to grain growth than the melted alloy. The dispersed phase AME205-899D and AME205-899E grades show unusual resistance to grain growth.

The alloy comparisons in Table 5 are only qualitatively accurate for metal deformation steps other than cold-rolling and can actually be quite misleading. Intermediate annealing of pans during a draw-anneal-draw sequence is an example and is illustrated in Figure 3 and Table 6. First and fourth draw untrimmed parts are shown in Figure 3, anneals being performed after the first, second, and third draws.

The part cross-sections are asymmetrical and the amount and nature of metal deformation varies widely at different locations on the part. Table 6 results for first draw pan-annealing indicate the difficulty in obtaining uniform annealed hardness without excessive grain coarsening with the non-dispersed phase AME200-899L alloy (best grain size results for etch grade is highlighted). ASTM grain sizes of #6 or coarser can result in tearing at the part corners (Point 2) upon redraw.

Surface cosmetics are also important on final parts as an ASTM grain size of #7 maximum is needed to keep orange peel (surface irregularities) within acceptable limits. Table 6 results clearly demonstrate the merits of the dispersed phase alloy and also show, when compared with Table 5, grain coarsening at lower temperatures for drawn parts than for cold rolled strip.

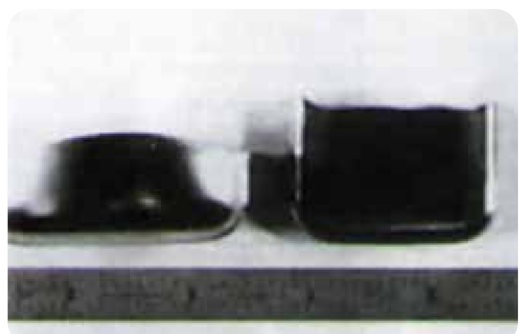


Figure 3. *First Draw (left) and Fourth Draw (right) Battery Casing Part from AME205-899D Alloy.*

Table 5. Grain Growth Comparisons

ASTM GRAIN SIZE AFTER INDICATED HEAT TREATMENT (^oF)						
NI Grade	**ASTM Grain Size Before 50% Cold Rolled**	**30 MIN./ 1200^oF**	**30 MIN./ 1450^oF**	**1 HR./ 1800^oF**	**1 HR./ 2000^oF**	**1 HR./ 2200^oF**
AME270-899A	7.5	7.0	7.0	7.0	2.0	2.0
AME200-899L	8.5	8.5	8.0	7.5	7.0	5.0
AME201-899M	8.0	8.0	7.5	7.5	7.0	5.5
AME205-899D	10.0	10.0	9.0	9.0	9.0	8.5
AME205-899E	10.0	10.0	9.0	9.0	9.0	7.0
AME205-899G	9.0	9.0	8.5	8.0	7.5	7.0
N02233	8.0	8.0	6.5	4.5	3.5	2.5
N02201	8.0	8.0	7.5	3.0	2.0	2.0

OXIDATION

Oxidation/reduction behaviour is important in perforated nickel used as an electrode substrate for slurry overcoating in high reliability Ni-Cd batteries. Predictable oxidation of the perforated substrate is required as is ease of oxide reduction during subsequent firing of the slurry-coated substrate. Field experience has shown AME200-899L to be a preferred grade as oxidation is predictable and the low level of stable oxide forming elements results in an oxide which is easy to remove in non-perforated tab portions of the substrate that are to be spot-welded.

SOFTENING TEMPERATURES

Softening temperature can be a very important parameter in component fabrication and/or assembly steps and will vary significantly for small chemical differences in high purity nickels. The temperature at which rapid softening of 50% cold-rolled AMETEK SMP alloys occurs ranges from a low and a high of 610 and 960^oF respectively, for AME270-899A and AME205-899E grades. Lower levels of cold-rolling will increase these cited Specialty Metal Products softening temperatures.

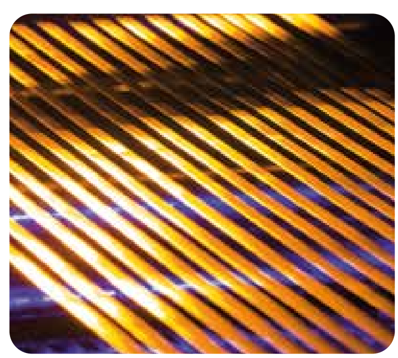


Table 6. First Draw Part Annealing Results

	HARDNESS (DPH)			ASTM GRAIN SIZE		
Part Condition	**Pt.1**	**Pt.2**	**Pt.3**	**Pt.1**	**Pt.2**	**Pt.3**
AME200-899L						
1st Draw	111	138	184	8.0	8.0	8.0
30 min @ 1100ºF	106	85	0.02	8.0	6.0-7.0	7.0
30 min @ 1100ºF	99	86	0.001	8.0	4.5-5.0	6.5
30 min @ 1100ºF	93	89	0.25	4.0	4.0	6.0
30 min @ 1100ºF	76	86	0.001	5.5	5.5	7.5
AME205-899D						
1st Draw	124	155	194	9.5	9.5	9.5
30 min @ 1100ºF	115	136	124	9.5	9.5	9.5
30 min @ 1200ºF	113	133	95	9.5	9.5	9.0
30 min @ 1300ºF	111	104	106	9.5	9.5	9.0
30 min @ 1400ºF	116	103	104	9.5	6.5-9.0	9.0

GRADE USAGE COMMENTS

Three AMETEK SMP grades, AME270-899A, AME200-899L, and AME205-899D, are currently used in different battery applications of which the author is aware. Grade AME270-899A finds limited use as a tab material in special applications. Grade AME-899L has more widespread use as a tab and perforated substrate in Ni-Cd batteries, and as cathodes, frames for expanded metal anodes and bus bars in lithium-thionyl-chloride batteries. Grade AME205-899D is used as deep-drawn casings, headers, and expanded metal for various lithium-based batteries.

Grades AME200-899L and AME205-899D are recommended herein. Grade AME205-899D is recommended over AME200-899L, where grain growth resistance is important or the higher strength of AME205-899D can be used to advantage in very difficult forming steps.

SUMMARY

The AMETEK SMP powder metallurgy strip process produces high purity nickel alloys which are uniquely suited for battery applications. Very low impurity levels are achievable and dispersed phase alloying approaches can be utilized to advantage. Tight control over low level alloying additions is also an inherent advantage of the process. As a result, additions in excess of that needed to routinely achieve a particular property are not required and addition impact on other properties is thus minimal. Two alloy grades, AME200-899L and AME205-899D, are described and recommended which offer the high electrical and thermal conductivities expected of high purity material coupled with the excellent formability and welding properties normally associated with more highly alloyed products.

SPECIFICATIONS

PHYSICAL PROPERTIES
(Typical handbook values for pure nickel)

DENSITY AT 70° F
8.90 g/cc; 0.322 lb./cu. in.

COEFFICIENT OF LINEAR EXPANSION
(IN./IN./°C)

20-100° C	0.000014
20-200° C	0.000014
20-500° C	0.000015
20-700° C	0.000016

YOUNG'S MODULUS, E, PSI X 10^{-6}
30.1

ELECTRICAL CONDUCTIVITY
22.6% IACS

ELECTRICAL RESISTIVITY AT 20° C
microhm, cm: 7.63
ohms/cir. mil./ft.: 45.9

THERMAL CONDUCTIVITY
cal./cm.2/sec. ° C/cm. at 70° C: 0.206
BTU/ft.2/hr./° F/ft. at 158° C: 49.9

TEMPERATURE COEFFICIENT OFELECTRICAL RESISTIVITY

20-100° C/°C	0.0058
20-500° C/°C	0.0074
20-800° C/°C	0.0060

ATOMIC NUMBER
28

ATOMIC WEIGHT
58.1

ATOMIC RADIUS (A)
1.25

CRYSTAL STRUCTURE
f.c.c.

LATTICE CONSTANT "a" (A)
3.52

MELTING POINT
1,453° C; 2,647° F

BOILING POINT
2,730° C; 4,950° F

LATENT OF HEAT FUSION
73.8 cal/g

SPECIFIC HEAT AT 20° C-BTU/lb./° F
0.105

ELECTRODE POTENTIAL
0.25 volts

VELOCITY OF SOUND
16,300 ft./sec.; 4,973 m/sec.

POISSON'S RATIO
0.31

THERMAL NEUTRON CROSS SECTION (BARNS)
Absorption: 4.6
Scattering: 17.5

CURIE TEMPERATURE
353° C; 665° F

MAGNETIC PROPERTIES
(Typical handbook values for pure nickel)

CURIE TEMPERATURE
353° C; 665° F

INITIAL PERMEABILITY
130

MAXIMUM PERMEABILITY
124

SATURATION INDUCTION, GAUSS (B)
6050

REMANENCE, GAUSS (B)
3250

COERCIVITY, OERSTEDS (H)
3.0

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