United States Patent Office 3,043,682 Patented July 10, 1962

3,043,682

LEAD-NICKEL-CADMIUM ALLOYS

Kenneth R. Grube, Hilliards, and Dean N. Williams, Columbus, Ohio, assignors, by mesne assignments, to The Bunker Hill Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Filed Feb. 19, 1960, Ser. No. 9,719
3 Claims. (Cl. 75—166)

This invention relates to lead alloys and, more particularly, to lead alloys containing nickel and cadmium as alloy additions.

This application is a continuation-in-part of our copending application Serial No. 724,225, filed March 27, 1958, now abandoned.

In the past, lead metal has been limited in its applications because of certain undesirable characteristics, particularly poor creep resistance. Poor properties in this respect limit the applicability of lead to many uses of other low-melting-point metals. Since lead at room temperature is at a higher absolute temperature relative to its melting point than is aluminum, for example, design stress limitations due to creep resistance are intensified. Such design stress limitations are dictated by creep resistance for lead then, whereas for aluminum, yield strength will dictate design stress limitations at room temperature. If the temperature, at which relaxation under applied stress occurs and where creep resistance, rather than yield strength, governs stress-resisting capabilities, could be raised, for lead, the metal could be used for applications not now available to it.

Lead alloys are used in a number of applications in which a material with exceptional resistance to corrosion is required. Examples of such uses include power and communication cable sheathing, liners for containers holding corrosive materials, and piping for chemical plants. Failure of the lead alloys in these applications is often traced to one of two distinct failure mechanisms, corrosion fatigue or creep. Corrosion fatigue is quite common in cable sheathing and piping when small cyclic stresses are imposed during service. The variation in peak service load in cable sheathing, for example, imposes one complete cycle of strain each twenty-four hours. Excessive creep is a principal mode of failure in tank liners and also is occasionally observed in the lead sheathing of oil-filled cables. Considerable improvement in service life would result in many lead alloy applications if resistance to creep and to corrosion fatigue could be obtained simultaneously without detriment to the other important properties of lead, such as ductility, weldability, formability, and corrosion resistance. The alloys of this invention accomplish this desirable result and in-plant service exposures have indicated that exceptional improvements over all existing lead-base alloys have been made.

It is, therefore, an object of this invention to provide alloys of lead possessing improved properties as compared with unalloyed lead and existing lead alloys.

It is a further object of this invention to provide lead alloys having greatly improved creep resistance as compared with unalloyed lead and existing lead alloys.

It is yet another object of this invention to provide lead alloys having good corrosion properties and bend properties as compared with unalloyed lead and existing lead alloys.

It is a further object of this invention to provide lead alloys having greatly improved creep resistance and bend properties as compared with unalloyed lead and existing lead alloys, while retaining good corrosion resistance.

Another object of this invention is to provide dispersions of nickel in an alloy of lead and cadmium, said dispersion-containing alloys having improved structural properties as compared with unalloyed lead.

Other objects and advantages of the invention will be

apparent from the following detailed description thereof.

In general, this invention comprises alloys of lead containing from about 0.3 to about 4.0 percent cadmium and from about 0.05 to 0.8 percent nickel, nickel being present as a dispersant and cadmium as a solid solution strengthener. Preferred ranges include from about 0.3 to about 2.0 percent cadmium and from about 0.2 to 0.8 percent nickel, balance lead. An optimum composition is about 0.2 percent nickel, 1.5 percent cadmium, balance lead.

The alloys of this invention may be prepared in any convenient way. For example, the dispersion-containing alloys may be prepared by adding the dispersoid to the lead melt. This is conveniently done by adding nickel powder to the lead melt or the lead-cadmium melt while stirring. In practice, a stirrer comprising a motor-driven steel rod on which were mounted opposite pitch propellers has been used. By adjusting the speed of the stirrer, it is possible to control the degree of agitation. The powder is drawn into the vortex created by the stirrer and, thus, enters the melt at the bottom of the vortex, thereby being dispersed uniformly throughout the melt.

For commercial production of the alloy the following procedure is recommended:

(1) Add nickel in finely divided form to molten lead leaving a temperature range of 750 to 850° F. If powdered nickel is used, it should be blown beneath the surface of the melt using an inert gas.

(2) Add cadmium in the form of ingot.

(3) Stir melt thoroughly during nickel and cadmium additions.

(4) A cover of ammonium chloride flux may be used to reduce surface oxidation and wetting of the nickel by the lead.

(5) Cast at a temperature near 750° F.

After alloying and casting into conventional ingot shapes, the alloys of this invention can be fabricated according to the usual procedures for lead alloys—extrusion, hot rolling, or cold rolling. The superior properties of the alloys are inherent in the composition, and when alloying is conducted as outlined above, subsequent processing can be carried out without difficulty. Sheet products from these alloy compositions are readily fabricated into a number of desired shapes. Welding of the alloys by conventional hot forming processes is possible and the properties of the alloy are not impaired by the welding process.

In evaluating the alloys of this invention, both creep-test measurements and bend-test results have been particularly noted. Creep results have been obtained by using both tension-creep and cantilever-beam creep tests. Bend tests have been carried out in an apparatus which subjects experimental specimens to one complete cycle of strain per minute. The number of cycles necessary to produce failure is recorded by means of rachet counters. Conventional tensile properties of the subject alloys have also been measured and are set forth as a part of the data in the tables which follow.

The mechanical properties of lead-nickel dispersion alloys are tabulated in Table 1. The data show that creep resistance increases with increasing nickel content up to about 0.4 weight percent nickel while good creep properties are obtained up to 0.8 percent nickel. This improved resistance to creep is obtained without any noticeable increase in tensile strength. The tensile data show that the strength remains almost constant with increasing amounts of nickel. Also, very little loss in ductility, as determined by the percentage of elongation, is apparent. In addition to improved resistance to creep a marked improvement of the resistance to cyclic bending is observed. About twice the number of bends (on the average) were required to cause rupture in the better

lead-nickel alloys than were required to rupture unalloyed lead. In one instance, a 300-percent increase in resistance to bending was noted. Analysis of the data indicates that as little as 0.05 percent nickel is beneficial.

Sn, and Cu. Tests were run at stresses of 300, 500, and 1000 p.s.i. Each specimen remained in test for 3000 hours or 3.00 percent extension, whichever occurred first. These results are included in Table 2.

Table 1.—Mechanical Properties of Lead-Nickel Dispersion Alloys Tested in the Extruded Form

Heat No.	Intended Ni content, weight percent	Elongation in two inches, percent	Ultimate tensile strength, p.s.i.	Creep data—76° F.					Bend data—One cycle per min., total number of bends to produce failure at 0.6 percent strain	
				Cantilever beam, deflection in 100 hr. at 1,000 p.s.i. inches	Tension, 300 p.s.i.-percent extension at end of—		Tension, 500 p.s.i.-percent extension at end of—			
					1,000 hr.	3,000 hr.	100 hr.	500 hr.	76° F.	110° F.
246	0			3.54	0.49	1.40	2.42		9,800	
272	0	71	1,870	4.00					9,800	
356	0	61	1,885	4.00					8,100	8,540
Average		66	1,880	3.84	0.49	1.40	2.42		9,230	8,540
230	0.04			3.80	0.21	0.28	0.85	2.90	9,536	
231	0.08			3.41	0.20	0.20	0.65	2.40	9,140	
288	0.12	68	2,020	2.85					11,752	
276	0.13	81	2,240	1.23					8,000	
290	0.13	76	2,100	1.43					10,445	
Average		75	2,120	1.84					10,066	
232	0.16			1.27			0.16	0.90	7,946	
233	0.23			0.86			0.16	0.80	8,940	
247	0.23			1.11			0.15	0.55	17,598	
248	0.23			0.86			0.27	0.70	10,734	
249	0.23			0.67			0.10	0.55	15,492	
250	0.23			1.10			0.18	0.75	16,776	
251	0.23			1.15			0.25	1.15	15,846	
273	0.23	75	2,260	2.80					10,584	
274	0.23	88	2,120	0.94	0.20	0.20	0.10	0.78	16,608	
277	0.23	66	2,120	0.52			0.10	0.65	19,028	
286	0.23	78	2,055	1.55	0.05	0.10	0.12	0.30	20,175	
287	0.23	65	2,075	1.07					17,886	
294D	0.23	59	2,120	0.73						
297	0.23	87	2,120	1.33						
298	0.23	78	2,120	1.73						
299	0.23	79	2,100	1.93						
367	0.23	79	2,100	0.60					16,354	7,358
371	0.23	75	1,930	0.28					18,992	10,845
374	0.23	75	1,950	0.40					15,230	9,642
449	0.23	80	2,130						11,548	
Average		76	2,100	1.09	0.125	0.15	0.16	0.69	15,254	9,282
369	0.32	83	2,000	0.46					18,048	19,612
372	0.32	75	1,990	0.38					22,034	15,939
375	0.32	76	2,000	0.45					14,226	9,814
Average		78	2,000	0.43					18,100	15,120
234	0.40			0.78	0.20	0.20	0.22	0.70	11,316	
370	0.40	78	1,975	0.34					31,512	17,530
373	0.40	69	1,965	0.29					30,342	15,672
376	0.40	73	1,930	0.15					27,108	16,766
Average		73	1,960	0.39	0.20	0.20	0.22	0.70	25,070	16,656
275	0.47	62	2,120	1.47					14,984	
278	0.47			0.55					12,307	
289	0.47	64	2,080	0.98					16,696	
292	0.47	69	2,160	1.03					17,150	
Average		65	2,120	1.01					15,284	
295D	0.48	56	2,130	0.85						
235	0.80				0.24	0.30	0.22	0.60	11,228	
339	0.80	71	2,170	0.28					11,659	16,152
Average		71	2,170	0.28	0.24	0.30	0.22	0.60	11,443	16,152
340	1.58	62	2,120	0.58					17,081	
341	4.10	107	2,230	0.92					20,440	

The dispersing of nickel powder in a solution-hardening alloy containing cadmium provides excellent and desirable properties. The presence of cadmium along with the nickel improves the quality of the dispersion formed by the nickel powder, thus permitting greater additions of nickel. Tensile strength can also be increased by the addition of cadmium to Pb-Ni alloys. No tendency toward agglomeration has been noted in Pb-Ni-Cd alloys containing as much as 0.48 and 0.78 weight percent of nickel.

Table 2 below lists mechanical-property data for Pb-Ni-Cd dispersion alloys.

Tension-creep studies made at room temperature indicate the good resistance to creep of the lead-cadmium-nickel alloys of this invention as compared with the base material (lead) or with prior art alloys containing As,

Studies indicate that, in general, resistance to failure by bending fatigue and resistance to creep at low stresses increases as the cadmium content increases up to about 2.0 percent. However, creep properties at higher stresses are a function of both cadmium and nickel contents.

The resistance to corrosion by sulfuric acid at 140° F. was determined for lead-nickel-cadmium alloys of this invention. Acid concentrations of 10, 20, 40, 60, 80, and 95 percent were employed. Temperature was maintained at 140° F. by means of a circulating hot water bath. A total exposure time of 144 hours was employed with weight measurements being taken at the end of 48-hour intervals. On the basis of the 144-hour test results, the corrosion resistance of the alloys of this invention appears to be somewhat superior to that of high purity lead. Detailed results are set forth in Table 2.

Hardness measurements made on a number of lead-cadmium-nickel alloys after aging at 75 and 150° F. indicate that the alloys do not show any appreciable tendency to age harden or overage during exposure at either temperature. Specimens were solution treated for 1 hour at 400 or 450° F. and water quenched before aging at 75 and 150° F. The hardness was measured at frequent intervals by the Brinnell method over a period of 8 weeks.

Table 2.—Summary of Mechanical Properties of Extruded Lead-Cadmium-Nickel Alloys

Melt	Intended composition (balance lead), percent			Tensile properties		Bend data—Total number of cycles to produce failure at 0.6 percent strain and indicated temperature		Tension creep data						
								Stress, p.s.i.	Percent deformation at end of indicated time, hr.					
	Cd	Ni	Cu	Elongation in 2 inches, percent	Tensile strength, p.s.i.	76° F.	110° F.		50	100	500	1,000	2,000	3,000
HIGH-PURITY LEAD														
246								300	0.10	0.13	0.33	0.49	0.92	1.40
								500	1.53	2.42	3.00			
								1,000	3.00					
291				69	1,955	13,800								
356				61	1,885	8,100	8,500							
441				57	1,975	13,500	7,500	300	0	0.05	0.05	0.15		
525				56	1,690	11,365	9,550	300	0.15	0.17	0.35	0.43	0.98	1.50
								500	0.76	1.15	3.00			
								1,000	3.00	3.00				
ARSENICAL LEAD														
282	0.16 As 0.13 Sn		0.05	70	2,260	32,500		300	0.01	0.02	0.07	0.11	0.16	0.20
								500	0.02	0.04	0.16	0.34		
								1,000	2.65	3.00				
304	0.13 Sn			56	2,260	35,475		1,000	1.80	3.30				
447	0.16 As 0.14 Sn 0.03 Bi		0.05	54	2,295	37,850	24,150	300	0.05	0.05	0.05	0.05	0.05	0.05
								1,000	3.00					
548	0.16 As 0.14 Sn			47	2,430	36,230	35,360	1,000	1.15	2.20	3.00			
468	1.00			51	3,430	53,150	42,225	300	0	0	0.40	0.80	[1] 2.0	
								500	0.30	1.30	3.30	3.00		
								1,000	1.95	3.00				
480	1.50			46	4,215	67,175	33,425	300	0.10	0.20	0.60	1.20	3.00	
								500	0.25	0.75	2.70	3.00		
								1,000	2.00	3.00				
466	2.00			42	4,300	36,275	32,100	300	0	0.05	0.10	0.20		
								500	0	0.05	0.35	0.68	[1] 1.50	
								500	0.20	0.25	1.25	2.95	3.00	
								1,000	0.30	0.50				
0.50 PERCENT CADMIUM PLUS NICKEL														
537	0.50	[2] 0.10		48	3,050	30,900	27,115	300	0.09	0.10	0.23	0.23	0.45	0.48
								500	0.10	0.13	0.30	0.43	0.70	1.00
								1,000	0.55	1.00	3.00			
								1,000	0.40	0.60	3.00			
538	0.50	[3] 0.10	0.05	48	2,880	23,850	31,900	300	0.05	0.05	0.15	0.18	0.20	0.25
								500	0.10	0.17	0.47	0.67	1.15	1.30
								1,000	0.40	0.80	3.00			
								1,000	0.55	1.05	3.00			
566	0.50	0.20		42	3,185	19,000	18,000	1,000	0.70	1.35	3.00			
								1,000	0.60	1.25	3.00			
403	0.50	0.23		48	3,085	22,000	18,300	300	0.05	0.50	0.10	0.10	0.10	0.20
								500	0.25	0.25	0.50	0.88	1.40	3.00
								1,000	0.90	1.50	3.00			
450	0.50	0.23		47	3,350	22,900	20,750							
1.00 PER CENT CADIMUM PLUS NICKEL														
358	1.00	0.08		35	3,720	30,025	13,950	1,000	0.45	0.75	3.00			
536	1.00	[4] 0.20		41	4,200	38,250	32,350	300	0.03	0.03	0.17	0.27	0.32	
						22,650	35,225	500	0.15	0.15	0.17	0.20	0.40	
								1,000	0.07	0.30	2.25	3.00		
529	[3] 1.00	[5] 0.20		43	3,770	24,700	24,775	300	0.10	0.13	0.17	0.20	0.20	0.21
								500	0.13	0.15	0.35	0.37	0.57	0.69
								1,000	0.50	0.77	2.20	3.00		
								1,000	0.15	0.25	1.50	3.00		
359	1.00	0.23		35	3,875	26,675	21,000	1,000	0.30	0.50	2.10	3.00		
404	1.00	0.23		39	3,620	31,500	36,500	300	0	0.05	0.05	0.10	0.10	0.10
								500	0.10	0.10	0.10	0.15	0.40	
								1,000	0.28	0.50	2.70	3.00		
539	1.00	[6] 0.20	0.05	41	3,925	43,950	20,800	300	0.10	0.10	0.20	0.23	0.30	0.35
								500	0.17	0.17	0.33	0.43	0.57	0.57
								1,000	0.30	0.50	1.35	2.61	3.00	
								1,000	0.05	0 10	0.90	2.32	3.00	
360	1.00	0.48		37	3,610	20,350	20,975	1,000	0.40	0.75	3.00			
							16,575							
							10,400							
361	1.00	0.78		41	3,745	23,750	22,400	1,000	0.40	0.60	2.50	3.00		
1.50 PERCENT CADIMUM PLUS NICKEL														
405	1.50	0.23		36	4,460	39,200	46,350	300	0.05	0.05	0.10	0.10	0.10	0.10
								500	0.05	0.05	0.05	0.05	0.10	
								1,000	0.10	0.20	1.10	2.15	3.00	
470	1.50	0.48		34	4,500	57,700	33,500							
471	1.50	0.48		34	4,300	58,275	28,300							

Table 2.—Summary of Mechanical Properties of Extruded Lead-Cadmium-Nickel Alloys—Continued

Melt	Intended composition (balance lead), percent			Tensile properties		Bend data—Total number of cycles to produce failure at 0.6 percent strain and indicated temperature		Tension creep data						
								Stress, p.s.i.	Percent deformation at end of indicated time, hr.					
	Cd	Ni	Cu	Elongation in 2 inches, percent	Tensile strength, p.s.i.	76° F.	110° F.		50	100	500	1,000	2,000	3,000
2.00 PERCENT CADIMUM PLUS NICKEL														
534	2.00	[7] 0.20	-------	47	3,625	52,400	34,250	300	0	0	0.07	0.07	0.11	0.20
						35,275	39,100	500	0.15	0.20	0.55	0.80	1.25	1.50
								1,000	0.65	1.40	3.00	-------	-------	-------
535	2.00	[8] 0.20	-------	52	3,575	72,400	62,100	300	0.10	0.10	0.18	0.20	0.25	0.30
								500	0.15	0.20	0.37	0.42	0.55	0.65
								1,000	0.45	0.85	3.00	-------	-------	-------
540	2.00	[9] 0.20	0.05	55	3,540	69,350	46,150	300	0.07	0.07	0.25	0.27	0.55	0.55
								500	0	0.02	0.03	0.05	0.25	0.50
								1,000	0.80	1.55	3.00	-------	-------	-------
469	2.00	0.23	-------	31	4,840	29,000	44,375	300	0.05	0.10	0.10	0.10	0.10	-------
								500	0	0	0	0	0	-------
408	2.00	0.48	-------	35	4,700	49,000	41,700	300	0	0	0	0	0	0
								500	0.05	0.05	0.05	0.10	0.10	-------
								1,000	0.05	0.05	0.10	0.18	-------	-------
								1,250	0.15	0.20	-------	-------	-------	-------
4.00 PERCENT CADIMUM PLUS NICKEL														
409	4.00	0.23	-------	47	4,540	61,500	59,500	300	0.05	0.05	0.05	0.10	0.10	0.10
								500	0	0.05	0.05	0.05	0.20	0.20
								1,000	0.25	0.50	2.70	3.00	-------	-------
410	4.00	0.48	-------	49	4,640	64,500	56,000	300	0	0	0	0	0	-------
								500	0	0	0	0	0	0
								1,000	0.10	0.10	[1] 0.45	0.80	-------	-------
								1,250	0.30	0.50	2.50	-------	-------	-------

[1] Approximately. [2] 0.13 actual. [3] 0.10 actual. [4] 0.08 actual. [5] 0.18 actual. [6] 0.24 actual. [7] 0.12 actual. [8] 0.19 actual. [9] 0.23 actual.

It will be apparent that new and useful lead-nickel-cadmium alloys having a unique combination of desirable properties have been disclosed. The alloys of this invention combine corrosion resistance, bend fatigue resistance, and creep resistance. These properties make the alloys especially useful for applications such as chemical processing equipment, and cable sheathing and for such other applications as collapsible tubes and battery grids. They are, indeed, useful for all applications requiring extreme resistance to strain rate bending and/or exceptional resistance to creep. Cable sheathing is an application utilizing their strain rate bending resistance, while their creep properties make them useful as nuclear shielding materials or as corrosion resistant sheathing for use in the chemical industry, or as pipe and conduit alloys.

New and useful alloys having been described and disclosed, it is desired to further define the invention in the attached claims.

What is claimed is:

1. Lead-base alloys consisting essentially of from about 0.3 to about 4.0 percent cadmium, about 0.05 to 0.8 percent nickel, balance lead, said alloys being characterized by greatly improved tensile strength, creep resistance, and bend resistance as compared with unalloyed lead.

2. Lead-base dispersion alloys consisting essentially of from about 0.3 to about 2.0 percent cadmium, about 0.2 to about 0.8 percent nickel, balance lead, said alloy being characterized by greatly improved tensile strength, creep resistance, and bend resistance as compared with unalloyed lead.

3. A lead-base alloy characterized by greatly improved tensile strength, creep resistance, and bend resistance as compared with unalloyed lead and consisting essentially of about 0.2 percent nickel, about 1.5 percent cadmium, balance lead.

References Cited in the file of this patent

UNITED STATES PATENTS

834,099	Allen	Oct. 23, 1906
1,645,098	Friedrich	Oct. 11, 1927
2,163,368	Betterton	June 20, 1939

FOREIGN PATENTS

666,856	Great Britain	Feb. 20, 1952