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MANGANESE ALLOY

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This invention relates to manganese alloys and is a continuation-in-part of my prior application, Serial No. 199,329, filed April 1, 1938.

The object of the invention is the production of improved alloys of manganese having very valuable properties over the entire range or within certain portions of the range to which the present invention relates, some of these alloys possessing unusual combinations of properties making them very desirable for certain purposes, as will be described. Detailed objects and features of the invention will be apparent from a consideration of the description which follows.

In my prior application I disclosed the composition of a relatively large number of ductile manganese alloys, indicating their hardness and strength in several states as well as other properties and their general usefulness in the arts. The present application is directed in the main, to high manganese alloys containing at least 60% manganese, but the proportion of manganese may run as high as 97% or even slightly above. The principal alloying constituents are copper and nickel employed together or alone with the manganese, with or without proportions of other metals having the effect of modifying in certain respects the characteristics of the alloy such, for example, as tin, aluminum or chromium.

The manganese employed is preferably a high purity manganese such as that made by the electrolytic method and containing not more than about 0.3% of impurities, and having the general composition disclosed in my application above referred to. Although some of the alloys of my invention may be made with manganese of a commercial grade having a somewhat greater proportion of impurities, in general to obtain uniform and maximum properties desired the high purity electrolytic manganese should be employed. This is particularly true of alloys containing a very high percentage of manganese such as above 85% or 90% manganese, for example, as I have found that it is impossible to produce a ductile alloy such as produced in accordance with my present invention unless the high purity electrolytic manganese is used.

A typical electrolytic manganese suitable for use in my invention throughout the range of alloying constitutents disclosed herein, contains in excess of 99.7% of pure manganese, approximately 0.27% to 0.28% sulfur (of which slightly less than half is present as sulfide) and approximately .015% of other impurities. The total proportion of silicon is in the neighborhood of .001%, while the carbon content is so small as to be non-detectable by ordinary methods of analysis. For best results in the practice of my invention, it is desirable that the total of carbon and silicon be less than .05%. Other impurities such as aluminum should preferably be kept to a minimum, it having been found that substantial proportions of aluminum as an impurity prevents obtaining suitable ductility in certain alloys, although in some cases, some slight proportions of aluminum may be added to the alloy with advantageous results.

While for some purposes the electrolytic manganese may be employed as it is obtained from the cells, for the most part it is preferable to desulfurize it by suitable methods. I have found that the sulfur may be reduced to .005% by appropriate treatment, such as by the use of easily reducible compounds of calcium, magnesium and lithium, including carbide, cyanamid, nitride or hydride, or alloys of calcium with other metals which are relatively volatile, such as magnesium, lithium, barium, etc. or with alloys of calcium, etc., with other metals, the presence of which is not detrimental in the finished alloy, such as calcium lead or lithium copper. Metallic calcium, magnesium or lithium may be satisfactorily used, but, due to their volatility at the temperature of molten manganese, their efficiency is not as great as that of the above mentioned compounds and alloys. The amount of desulfurizing material used depends on the sulfur content.

By treatment to remove sulfur, the purity of the manganese may be brought to above 99.9%. Such a raw material may be used to produce excellent alloys which cannot be successfully produced by the use of so-called commercial grades of manganese.

Among the properties obtainable in the alloys of my present invention are high modulus of elasticity, the property of being hardened by cold work and by heat treatment, the property of having a high co-efficient of expansion, the property of high electrical resistance, in many instances with extremely low temperature co-efficient, and remarkable vibration damping capacities. While the maximum value of these various properties does not lie in identically specific ranges throughout the range to which the present invention relates, some of the properties do lie in the same range or have their peaks within the same range whereby unusually desirable combinations of properties are obtainable. In general, however, the properties referred to are present over the entire range of alloys described in the present application so that the quantities of various characteristics may be so combined as to produce unusual combinations of properties in making it possible to employ the alloys of the present invention to very great advantage for a relatively large number of uses.

For convenience, I shall describe the invention by reference to the various properties discussed and show in general the ranges in which these properties are obtainable.

I have found, for example, that certain manganese alloys possess a modulus of elasticity higher than any of the common non-ferrous metals or alloys. As is the case with iron, I find that this modulus is an intrinsic property of the metal itself and is high in all manganese alloys of the present invention, but is particularly pronounced in alloys containing 70% or more manganese. I interpret this to mean that alloys containing more than this percentage of manganese contain a substantial proportion of a constituent which is either gamma manganese or a solid solution of some other metal or metals in gamma manganese. The following illustrates the modulus of elasticity of several alloys to illustrate my invention.

TABLE 1

Modulus of elasticity of ductile manganese alloys made with high purity manganese

Mn	Cu	Ni	Other	Modulus lbs.X10⁶ per sq. in./in.
97	2	1	------	28.2
92	5	3	------	27.1
85	15	5	------	27.5
80	20	------	------	20.0
75	16.7	8.3	------	29.0
70	20	10	------	27.3
70	19	10	Sn 1	27.8
70	25	5	------	25.0
85	15	------	Zn 5	23.1
54	37	8.5	------	16.2
60	40	------	------	12.0
47	42	------	Zn 11	13.6
30	55	------	Zn 15	14.0
90	8	1	Cr 1	28.7
30	50	5	Zn 15	13.3

The uses of a manganese alloy having the high modulus of elasticity will be apparent when the other properties of these alloys are disclosed.

I have found, for example, that these manganese alloys may be obtained with varying tensile strength, elongations and yield points by suitable cold work and heat treatment. I have illustrated my invention in this regard in the following table:

TABLE 2

Mechanical properties of ductile manganese alloys made with high purity manganese

Composition				Cold Worked			Annealed		
Mn	Cu	Ni	Other	Tensile strength	Yield point	Elongation	Tensile strength	Yield point	Elongation
92	5	3	------	95,000	40,000	2	68,500	None	35
90	10	------	------	115,000	52,000	1.5	78,000	None	25
80	20	------	------	85,000	41,000	2	62,000	None	26
80	------	20	------	105,000	46,000	1.8	74,000	None	42
75	16	9	------	85,600	40,000	2	63,000	None	25
70	20	10	------	106,000	44,000	2	72,000	None	31
70	25	5	------	95,800	38,000	2	67,000	None	33
75	20	5	------	82,000	37,000	2	62,000	None	35
60	40	------	------	78,000	35,000	2	51,000	28,000	21
54	37	9	------	92,000	38,000	2	59,000	24,000	26
47	42	------	Zn 11	109,000	43,500	2	73,000	32,000	38
30	55	------	Zn 15	81,600	36,500	2	63,000	19,000	24
30	50	5	Zn 15	118,000	51,000	2	73,000	24,000	29

An examination of the data in this table in comparison with that in Table 1 shows that the alloys which possess a modulus of 20,000,000 or more are those which have no definite yield point in the annealed state.

This further confirms my main classification of alloys containing more than 60% manganese as having a substantial proportion of a constituent having new and useful properties. The very considerable difference between yield point and tensile strength for all of the alloys in this table illustrates the useful property of great work hardening which they possess.

I have also found that manganese alloys within the range of my invention possess remarkable and useful co-efficients of thermal expansion. I have illustrated my invention in this regard in the following table:

TABLE 3

Coefficient of expansion of ductile manganese alloys made with high purity manganese

Mn	Cu	Ni	Other	Hard drawn	Annealed
97	3	2	------	18.0×10^{-6}	24.7×10^{-6} cm./cm./° C.
92	5	3	------	19.1	25.3
85	10	5	------	20.3	21.4
90	10	------	------	18.0	21.6
80	20	------	------	25.5	27.9
75	16.7	8.3	------	28.3	26.4
70	20	10	------	26.5	26.0
60	40	------	------	23.6	23.6
54	37	9	------	21.4	21.8
80	------	20	------	19.8	19.0
75	20	5	------	27.2	26.6
47	42	------	Zn 11	19.0	23.5
70	19	10	Sn 1	23.1	23.6
90	8	1	Cr 1	16.5	18.2
30	50	5	Zn 15	19.0	18.3

From this table, it will be seen that the hard drawn alloys show co-efficients of expansion as high as 28.3×10^{-6} centimeters per c. m. per degree centigrade and the annealed alloys have co-efficients as high as 26.6. It will be observed that the highest coefficients do not occur in alloys of the highest manganese content, but in alloys containing from 60 to 80% manganese.

While coefficients as large as those I have found for the 60 to 80% manganese alloys are known for the soft metals like zinc and lead, they have not heretofore been observed in alloys having at the same time a modulus of more than 20,000,000 and a yield point of more than 20,000 pounds per square inch. The usefulness of such combination properties will be evident but I may illustrate it by the construction of bi-metal strips for thermostats. Such strips have heretofore been commonly made of such materials as brass and nickel steel. My invention provides an improvement over brass in this use, alloys of my invention having a 50% greater expansion and a considerably greater modulus and yield point than any of the brasses. It will be clear that the contact pressure which can be exerted by a given thickness of strip is determined by the modulus and that my invention therefore provides a superior thermostatic metal.

I have also found that the electrical properties of alloys made in accordance with my invention are new. In the following table, I have illustrated the specific electrical resistance of the alloys in the hard drawn and annealed state and their temperature coefficient for the annealed state.

TABLE 4

Electrical resistance of ductile manganese alloys made with high purity manganese

Mn	Cu	Ni	Other	Specific resistance		
				Hard drawn	Annealed	Temp. coeff. ohms/100° C.
97	2	1	--------	93	102	30
92	5	3	--------	108	112	21
90	10	--------	--------	128	152	15
85	10	5	--------	152	161	12
80	20	--------	--------	178	169	10
80	--------	20	--------	162	156	8
75	16.7	8.3	--------	182	182	4
70	20	10	--------	196	203	0
60	40	--------	--------	214	194	0
54	37	9	--------	189	193	12
70	25	5	--------	183	181	2
75	20	5	--------	168	163	3
47	42	--------	Zn 11	176	163	15
30	50	5	Zn 15	132	115	18

It will be seen that the specific resistance has values of more than 200 for certain alloys which also have a substantially negligible temperature coefficient. The composition range having this useful combination of properties is from 60 to 80% manganese, that is, the same range having a high temperature coefficient of expansion. It would be predicted that alloys within this range made in accordance with the known art would not possess this desirable combination of properties but would have a specific resistance below 140 and a very much greater temperature coefficient.

I have found that several of the alloys studied show an increase in resistance on annealing the cold worked alloy. This is observed to some extent in alloys containing more than 60% manganese and is thought to be a property of the special constituent postulated to exist in alloys above this composition.

The usefulness of alloys with high electrical resistance and low temperature coefficient is quite great. The alloys made in accordance with my invention possess these properties and at the same time have a high coefficient of thermal expansion which makes them useful for electrical control purposes where the heat produced by the electric current is used to bring about expansion and make or break a connection.

I have also found that certain alloys made in accordance with my invention possess a higher vibration damping capacity than heretofore found in alloys having relatively high strength, yield point and modulus. This property is indicated by the lack of metallic ring in alloys containing substantially more than 60% manganese. In order to generally quantify this effect, I have measured vibration damping capacity according to the resonance method and have recorded the results in the following table:

TABLE 5

Damping capacity of manganese alloys

Composition				$h \times 10^{-3}$ Loss in ergs per cycle per unit volume per unit strain squared
Mn	Cu	Ni	Other	
85	10	5	--------	200
80	20	--------	--------	92
75	16.7	8.3	--------	32.2
70	20	10	--------	12.2
60	40	--------	--------	99.6
90	10	--------	--------	182
91.9	4.8	3.3	--------	212
54.3	37.2	8.5	--------	10.04
47.2	42.1	--------	Zn 10.4	10.18
28.2	55.9	--------	Zn 15.9	7.39
31.6	48.4	4.9	Zn 15.1	7.82
72.0	22.7	5.3	--------	9.2
75.6	19.2	5.2	--------	13.8
79.2	--------	20.8	--------	16.26

For purposes of comparison, I have found that the damping capacity of steel is 1.5–20. I have observed that hardening by either cold work or heat treatment is substantially without effect on the vibration damping capacity of my novel alloys. Alloys having a high damping capacity together with the modulus, strength and yield point of these alloys may be used to form gears, cams and other machinery elements where noise is objectionable.

In my copending application, I disclose the hardening of alloys composed essentially of gamma manganese by heat treatment. I postulated that this hardening was due to the transformation of part of the gamma manganese into a lower temperature stable form so that very fine hard particles of this form of manganese were dispersed through a matrix of gamma solid solution. This hardening may take place in any manganese alloys which may be maintained in the ductile state by quenching and which contain insufficient alloying element to render the gamma form stable at room temperature. As I also disclosed in my copending application, the hardening may be so great in some of these alloys as to produce a brittle and useless alloy. I have found that the coordinate hardness and toughness of these alloys is determined not only by their composition but by the temperature from and to which they are quenched, the rate of quenching, the temperature and time of reheating, and the rate of cooling from the reheating step as well as the presence or amount of cold work between the quenching and reheating step. It will be obvious that with so many variables I can only indicate by a few examples the direction in which changes in these conditions affect the final properties of the alloys. It is interesting to note that the dimension change in hardening is very small, being of the order of 2.8×10^{-4} cm./cm.

Table 6, which follows, indicates in general the effect of composition on the hardening with a fixed quenching temperature of 1100 degrees C., a water quench, reheating for two hours at 700 degrees C. and water quenching. The change in other physical properties is also indicated.

TABLE 6

Hardening of ductile manganese alloys

	Quenched					Hardened 700° C.							Annealed 800° C.				
	H.	T. S.	Mod.	Ex.	Res.	H.	T. S.	Y. P.	Mod.	Ex.	Res.	H.	T. S.	Mod.	Ex.	Res.
1	^{b}92	68	28	18	128	^{c}50	200	87	28	16	103	^{b}90	68	28	25	102
2	^{b}66	54	27	------	------	^{c}45	187	78	27	------	------	^{b}90	68	27	25	112
3	^{b}70	56	26	------	------	^{c}52	208	88	26	------	------	^{b}72	------	26	------	------
4	^{b}80	63	------	------	------	^{b}87	70	None	------	------	------	^{b}80	63	------	------	------
5	^{b}79	61	------	------	------	^{c}10	85	33	------	------	------	^{b}83	65	------	------	------
6	^{b}80	62	20	------	------	^{b}95	71	None	20	------	------	^{b}80	62	20	------	------
7	^{b}88	67	29	26	182	^{b}86	66	None	29	26	182	^{b}86	66	29	26	182

(The yield point for the quenched and annealed samples given above was very low (substantially none) in each instance).
The numbers at the left of the above table stand for alloy samples as follows:

(1) 97 Mn 2 Cu 1 Ni
(2) 92 Mn 5 Cu 3 Ni
(3) 95 Mn 5 Cu
(4) 90 Mn 10 Cu
(5) 85 Mn 10 Cu 5 Ni
(6) 80 Mn 20 Cu
(7) 75 Mn 16 Cu 9 Ni

In reading the table, the abbreviations are to be interpreted as follows: "H." stands for hardness on the Rockwell scale; "T. S." stands for tensile strength; "Mod." stands for modulus in units shown in Table 1; "Ex." stands for coefficient of expansion in the units shown in Table 3; "Res." stands for specific resistance, as expressed in Table 4; and "Y. P." stands for yield point.

Slower rates of quenching as in oil or air stream give lower hardness and greater toughness on reheating. Quenching directly into a salt bath at 500 to 700 degrees gives greatly increased toughness with some lowered hardness. Slow cooling from the reheating step increases toughness. Cold work between the quenching and reheating step greatly accelerates hardening and in some instances produces much greater hardness. This is to be expected because the hardening temperature is not sufficient to remove the hardening by cold work.

In general, a temperature of 800 degrees is required to bring about definite softening of the hardened alloy and a higher temperature is required for full anneal. As an example of the effect of reheating temperature on hardness I give the following results:

Alloy comp. Mn 92,
Cu 5, Ni 3____Quench R_b68. Heat 500° R_b93.
Heat 600° R_c38. Heat 700° R_c45.
Heat 800° R_b90.

The density of these alloys is substantially less than that of steel being from 7.0 to 7.2.

In the above table, "R_b" stands for hardness on the Rockwell B scale, and "R_c" stands for hardness on the Rockwell C scale.

In my copending application, I have disclosed the formation of a tenacious hard case on alloys high in manganese by heating in ammonia at 500° C. I have found that the alloys which are capable of hardening by heat treatment can be successfully case hardened in this way.

In my copending application, I have disclosed the chemical properties of certain manganese alloys. The alloys of my present invention behave in general like solid solutions in which the parting limit occurs at an unusually low percentage of the added element; that is, the surface atoms of manganese are attacked by the etchant and a continuous layer of the more noble metal, e. g. copper or nickel, is exposed so that the attack does not proceed further. This layer of more noble metal is extraordinarily continuous and remains intact with further rolling or drawing operations on the alloy. The advantages of such copper, nickel or zinc clad alloys will be evident.

The proportion of alloying constituents for alloys of manganese hardenable by heat treatment varies somewhat, and in general the following tabulation is a guide to at least the proportion of elements which are required to produce a definite pronounced hardening under heat treatment:

Alloying elements	Composition
	Percent
Copper	2- 8
Nickel	8-10
Copper plus nickel	Cu 2-10 Ni 1- 5
Copper plus Al	Cu 5-10 Al 1- 3
Copper plus zinc	Cu 5-10 Zn 1- 3

This table is not in any sense complete, particularly as to ternary and quaternary alloys, nor does it include all possible factors, it being obvious that constituents of ternary alloys cannot be plotted along a straight line. In the case of nickel alone, for example, some hardening occurs when as much as 20% nickel is used, but the most pronounced hardening occurs in the neighborhood of the range indicated.

The characteristics of the alloys of the present invention are further evidenced by their remarkable ductility in both the quenched and fully annealed states. I have found that alloys of high manganese content produced from relatively impure grades of commercial manganese, which show considerable ductility (at least some of them) in the quenched state, develop brittleness when subjected to heat treatments which fully anneal and soften similar alloys when made in accordance with my invention.

For the most part, the preceding description is concerned at any given point with only a single property of the alloys of my invention, but by the use of the tables the ranges in which desirable combinations of properties may be obtained will be made clear. There is a definite range, however, within which all of these properties may be found in some cases to quite a pronounced degree in a single alloy. Most of the alloys of my present invention contain at least 60% of manganese, at least one of the elements copper, nickel and zinc, and in some cases one or more of the elements tin, aluminum and chromium. Either copper or nickel may be used alone in proportions as high as 40%; zinc, preferably employed with one or both of the elements copper and nickel, may be used in proportions as high as 30%; while tin, aluminum and chromium, generally, should not be present in proportions greater than about 5%; and if more than one of the latter group of metals is present, the total amount of such group should not be appreciably greater than 5%. The ranges in which the properties discussed above are for the most part present are those ranges in which at least 70% of manganese is employed, except in the instances, as pointed out, where the proportion of manganese may be as low as 60% or somewhat below.

There are a very large number of uses for the alloys of my present invention where the unusual properties or combinations of properties discussed can be taken advantage of. They include all uses where high tensile strength, vibration damping properties, machinability, high temperature co-efficient and other properties discussed are desired alone or in combination. Examples are thermostatic elements, electrical resistances, heating elements for low temperature sealed units, spring material, fabricated parts subjected to strain, gears, sprockets, chains, ratchets, pawls, and other transmission elements where vibration is objectionable, artillery parts where sound deadening is required, supporting members for punching dies and similar purposes to deaden sound, non-magnetic machine parts of adequate strength, poppet valves and seats in gas engines, and other uses.

In connection with the vibration damping capacity, it may be noted that this capacity begins to fall off rather sharply above temperatures of about 100 degrees C. There are many instances where the vibration damping capacity for these alloys may be used where it would be substantially at room temperature, however, such as in the production of organ pipes and musical instruments where wood and lead are commonly used, and for such uses as acoustic filters made, for example, by perforating plates of the alloy and arranging them in the form of a filter. The low thermal conductivity and high reflection together with the ability to roll thin sheets makes it possible to produce good insulation and sound proofing structures in built up units of metal foil in the manner in which aluminum is sometimes used. Propeller blades of all sort for fans, boats and the like may be produced by the use of suitable alloys coming within my present invention.

The uses given are entirely illustrative, but it is clear that the alloys of my invention may be employed for many purposes where non-ferrous alloys have heretofore been considered of no value, and in the cases where my alloys would replace non-ferrous alloys they have properties not ordinarily found in non-ferrous alloys.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. An alloy having high vibration damping capacity comprising at least 1% nickel, at least 2% copper, and the balance being substantially all manganese, the manganese constituting at least 95% of the alloy.

2. An alloy having high vibration damping capacity comprising about 1% nickel, about 2% copper, and about 97% manganese.

3. An alloy comprising from 1% to 10% nickel, from 2% to 20% copper, and the balance being substantially all manganese, the manganese constituting from 80% to 97% of the alloy.

REGINALD S. DEAN.