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ALLOY HAVING HIGH ELASTIC STRENGTHS

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This invention pertains to an alloy which may contain cobalt, chromium, nickel and other metals; and which can provide a non-corrosive body of low or non-magnetic properties, and capable of exhibiting very high strength properties. While it is preferred to have the major proportion of the alloy constituted of cobalt, chromium and nickel, molybdenum is also preferably present along with carbon, iron, manganese, and beryllium. Insignificant amounts of still other elements may be present.

This application is a continuation-in-part of our parent application Serial No. 567,894, filed December 12, 1944, on "Cobalt-Chromium-Nickel-Base Alloy," now abandoned.

It has been discovered that the present alloy has unusual properties, and extensive tests have shown its suitability for use under the exacting conditions of springs which are under maintained loading in service, such as watch mainsprings and other power springs, and for other purposes where its chemical and physical properties are desirable.

Power springs are of necessity under maintained load during operation, which load may attain an over-all stress condition closely approaching the maximum allowable under static tests; and above all present the problem of storing a maximum of available energy in a minimum space. Such springs have been generally made of plain carbon steel with carbon contents in the range of about 1.00 to 1.30 percent. In practice, it is necessary to heat the tape of approximately spring width and thickness to a relatively high temperature and quench it, usually in oil, to develop the desired hardness. This heating may modify the surface composition of the steel and generally roughens the surface in addition to producing an oxide coloration. After hardening, the stock must be polished in order to produce a smooth surface. The hardened tape is too brittle for use as a power spring and must be reheated or tempered to develop sufficient toughness for practical applications. This again produces a discoloration.

In addition to the difficulties just mentioned, there are many others connected with the heat treatment of steel springs. The hardening process is highly critical in regard to the temperature and the time at the hardening temperature. If the temperature is too low or the time too short, the spring will be soft and cannot be used. On the other hand, if the temperature is too high or the time at temperature too long, the steel may

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develop a coarse grain and be too brittle, even after tempering, for use as a power spring.

Even when these carbon steel springs and other articles have had what would be considered as the best possible heat treatments, they are lacking in certain desirable characteristics such as corrosion resistance and high-yield strength or creep resistance, and they are magnetic. It is well known in the trade that many, and probably the greater number, of the breakages in power springs result from corrosion of the steel. Even tiny rust spots materially reduce the section of a spring, and it is well known to engineers that corrosion pits can serve as stress raisers and thus lead to early failure by a combination of corrosion and fatigue.

Failure of a spring by breaking is serious, but in normal times the spring can be replaced at relatively low cost. However, steel springs are characterized by a more serious defect from the standpoint of a correct timekeeper. This defect is known in the industry as "taking a set" and might properly be defined by engineers as "creeping" or showing continued deformation in service. A power spring which "sets" in service, upon repeated stress and release, loses its power to drive the associated device under the selected original conditions, and, as a result, the drive no longer operates satisfactorily. Under such circumstances, it is impossible to correctly adjust and standardize the device in the factory. This characteristic of "setting" or "creeping" of power springs results from the material having too low values of such properties as proportional limit and yield strength.

The problem of developing high elastic properties and, at the same time, adequate resistance to breakage is a most difficult one and has confronted industry for many years. It has, for example, become somewhat more serious as the demand for smaller watches has increased. If a watch mainspring is exposed to a magnetic field, the steel becomes magnetized and the watch no longer keeps the correct time, and it may not run at all: like troubles arise with other devices where magnetic fields are present and carbon steel parts are present.

A limited number of special alloy watch mainsprings have heretofore been used. One such alloy is of nickel-iron-chromium base with smaller amounts of molybdenum, manganese, and beryllium. The type analysis is represented by 60% nickel, 15% chromium, 15% iron, 7% molybdenum, 2% manganese, and about 0.6% beryllium. Such an alloy has improved corrosion resistance,

because of its chromium content, as compared with the carbon steels. Tests on an alloy of this type and on commercial mainsprings made of such an alloy have shown that the elastic properties, such as proportional limit and yield strength, are not adequate for watch mainsprings; in fact, the elastic properties were found to be inferior to steel mainsprings of commercial production. Tests also showed that the beryllium content is critical and must be controlled within close limits, which is difficult in melting and otherwise processing the alloy.

Consideration has been given to the use of certain stainless steels, such as an alloy of about 18 percent chromium—8 percent nickel, in the cold worked condition. While such an alloy has considerable resistance to corrosion, it is low in mechanical properties and does not have the high proportional limit and high yield strength necessary for watch mainsprings. Its modulus of elasticity in the cold-worked condition is also low, and such an alloy steel cannot be hardened sufficiently by the heat treatments used on the ordinary carbon steel springs but it is necessary to rely upon cold working to develop high strength.

Consideration has also been given to alloy spring steels, such as those designated as SAE 6150, SAE 9250 and SAE 9260. While these alloy steels are highly successful in certain of the larger machine springs and where abundant space is available for them, they require a high temperature for hardening which results in surface oxidation; and such steels have not been found satisfactory for thin sections, for example .004 inch in thickness, and even thinner, as employed for watch mainsprings and in other devices which afford only a small space for the part.

Thus many deficiencies have been found in the materials which have been used or tried in the production of power springs, and a purpose of the present invention is to overcome most of these deficiencies and to result in an improved power spring or other article.

It is, therefore, one object of our invention to provide an improved power spring alloy. A more specific object of our invention is to develop a superior spring alloy for chronometric instruments, such as mainsprings for watches.

It is a further object to develop an alloy having high elastic properties, such as proportional limit, yield strength, and modulus of elasticity.

A further object is to develop an alloy which is highly resistant to corrosion in such applications as mainsprings in watches, etc.

Still a further object is to develop an alloy which is essentially non-magnetic.

Another object is to develop an alloy which is readily workable into spring sizes and shapes, including those used for watch mainsprings.

Yet another object is to provide an alloy which is highly resistant to creep or to taking a permanent set in service as a spring.

Another object is to provide an alloy which is capable of developing the high elastic properties desirable in springs without the use of closely-controlled high-temperature heat treatments as required for steel springs.

Another object is to provide an alloy having the best possible combination of the desirable properties essential to watch mainsprings.

Another object is to provide a power spring manufactured from a cobalt-chromium-nickel-base alloy.

Other objects and accomplishments of the in-

vention will be more clearly brought out in the following specification and in the appended claims.

We have discovered that combinations of cobalt, chromium, nickel, molybdenum, carbon, and beryllium, in certain selected amounts, produce an alloy which is highly suitable for the production of improved watch mainsprings. In addition to the above-mentioned metals, the alloy preferably contains iron and manganese and may contain insignificant amounts of other elements such as silicon. The desirable features of this alloy have been confirmed by extensive tests, including tests in watches.

Cobalt in the alloy of this invention functions to strengthen the alloy and to improve its response to the age hardening treatment. While cobalt may be used in the range of 20 to 50 percent, the preferred range is 28 to 45 percent. At around 45 to 50 percent, the alloys are inclined to be too brittle and are difficult to cold-roll; and with 28 to 20 percent, the alloys are inclined to be too low in strength for some applications.

Chromium is relied upon for corrosion resistance, and it has been found desirable to use at least 15 percent of chromium and preferably over 20 percent of chromium to develop adequate corrosion resistance. On the other hand, difficulties are encountered in melting and otherwise processing of the alloys when the chromium content is too high, but alloys containing up to 30 percent chromium have been produced and studied. The preferred range is from 20 to 26 percent of chromium. Increasing the chromium beyond 30 percent does not materially further improve the corrosion resistance of the alloy.

Nickel is preferably at 15 to 30 percent, and has been used in the range of about 5 to over 30 percent and can be used to even higher percentages. Nickel and iron are to some extent supplementary to each other, although the most satisfactory results are obtained with alloys which contain more nickel than iron. It has been found that the sum of the nickel plus iron and manganese is usable in about the range of 20 to 50 percent, and the preferred amount of nickel plus iron is in the range of 25 to 42 percent. Preferably under 15 percent of iron is present. Alloys containing iron above about 18 percent, have been found to be unsatisfactory because of decreased resistance to scaling when heated, and because of poor cold-rolling characteristics.

Beryllium is a desirable constituent of the alloy, and appears to give improvement to certain alloys in the strength properties on aging after a quenching treatment, more particularly on aging after a quench-anneal and cold reduction. It has been found that in an alloy of this type, relatively small amounts of beryllium are sufficient to add important properties to the alloy, and amounts as low as .01 percent have been found to add materially to its response to hardening and strengthening by an aging treatment after quenching and cold rolling. Highly satisfactory results have been obtained by beryllium contents in the range of .02 to .05 percent. But with low-carbon contents, there are advantages in using more beryllium, to about .09 percent. It is one of the features of this invention that the beryllium content required in the alloy is much lower than that found necessary in certain nickel-base alloys which have been used for watch mainsprings. For example, in one previously used alloy containing over 50 percent nickel, the beryllium content was of the order of 0.5 to 0.6 percent and might be as

high as 1.0 percent. However, in the present alloy employing beryllium, 0.02 to 0.05 percent of beryllium is generally adequate, and it is preferable to use beryllium contents under 0.09 percent, because no improvement in the final mechanical properties has been found to result from the use of a higher beryllium content, and using a higher beryllium content adds to the cost of the alloy and also presents problems in hot and cold roll-

ing, and scaled badly during heating for hot rolling, and has been included to indicate one effect of departure from the conditions claimed.

The other alloys are to be considered as merely illustrative and are not to be interpreted as limiting or as covering the entire range of usable alloys. Compositions outside of those listed have been used with good results, and this applies to all, or practically all, of the elements listed.

Table 1.—Illustrative alloy compositions and properties

Alloy No.	Chemical Composition, Per Cent								Condition or Treatment	Mechanical Properties (1)				Hardness, Vickers
	Co	Cr	Ni	Be	Mo	C	Fe	Mn		T. S.	P. L.	Y. S.	Modulus	
1-----	40.0	20.0	15.5	*.02	7.0	.15-.20	15.0	2.0	{Cold rolled.....	294	117	142	27.6	535
									{Aged (2).....	373	266	290	28.8	690
2-----	40.0	25.0	15.0	*.01	7.0	.15-.20	10.0	2.0	{Cold rolled.....	314	125	153	27.7	535
									{Aged (2).....	395	251	290	29.6	640
3-----	30.0	26.0	31.0	*.05	6.0	.15-.20	7.0	1.0	{Cold Rolled.....	271	174	198	23.5	482
									{Aged (2).....	339	240	280	29.4	573
4-----	35.0	25.0	20.0	*.03	7.0	.15-.20	11.5	1.5	{Cold Rolled.....	272	155	178	22.3	516
									{Aged (2).....	347	202	290	30.0	623
5-----	35.0	25.0	30.0	*.03	7.0	.15-.20	1.5	1.5	{Cold Rolled.....	284	135	164	26.2	481
									{Aged (2).....	358	207	269	30.9	579
6-----	40.0	25.0	22.0	*.03	Nil	.15-.20	10.0	2.0	{Cold Rolled.....	263	142	175	24.1	466
									{Aged (2).....	321	190	228	29.7	486
7-----	35.0	25.0	5.0	*.03	7.0	.15-.20	26.0	2.0	Too brittle for cold rolling					
8-----	*39.8	20.0	15.5	*.02	7.0	*.05	15.0	*1.89	{Cold Rolled.....	259	134	169	22.4	519
									{Aged (2).....	326	193	243	29.5	635
9-----	40.0	20.0	16.5	*.02	7.0	*.11	15.0	*0.55	{Cold Rolled.....	261	131	160	23.7	536
									{Aged (2).....	331	218	253	30.0	678
10-----	40.0	20.0	15.5	*.03	7.0	*.09	15.0	2.0	{Cold Rolled.....	262	135	165	23.4	531
									{Aged (2).....	341	219	259	29.4	681

ing and in adequate solution of the excess of the beryllium compound in the heat-treating operations.

Carbon must be kept within certain composition ranges, because when the carbon is too high the alloy is inclined to be brittle and, furthermore, it will not stand the desired amount of cold reduction without showing excessive breakage. The usable range for carbon is about 0.05 to 0.30 percent, and highly satisfactory results have been obtained in alloys containing about 0.10 to 0.20 percent. Carbon functions to strengthen the alloy and also aids in its response to precipitation hardening.

Molybdenum is preferably used in the amounts of about 6 to 7 percent. When 3 percent or less of molybdenum is used, the alloy is somewhat lower in strength than when larger amounts are employed, and there is no substantial improvement in the ductility; with such low-molybdenum alloys, it is advisable to employ the upper ranges of beryllium content. The range for molybdenum is about 1 to 10 percent, for articles of high strength values.

Manganese is usually present in amounts up to about 3 percent, preferably about 0.5 to 2 percent, and it is considered as one of the additional elements which behaves like nickel in improving the alloy in its performance during hot and cold rolling.

A specific alloy containing 40 percent cobalt, 20 percent chromium, 15.5 percent nickel, 15 percent iron, 0.03 percent beryllium, 7 percent molybdenum, 2 percent manganese, and about 0.15 percent carbon, has been found excellently adapted for the requirements of watch mainsprings, and responds excellently to the mechanical and heat treatments.

Alloy compositions, with their properties, are shown in Table 1, with this table including one composition (alloy No. 7) which is outside of the range of the invention, in containing 26 percent of iron with 5 percent of nickel, and which was found to be too brittle for satisfactory cold roll-

Table 1 is set up on the general basis of proportion of substance introduced in preparing the alloy; but for the items marked with an asterisk (*), the percentage represents chemical analytic result. In this respect, the content of beryllium was analytically determined in all alloys because of its importance and to show that the desired amount was present in the alloy. Chemical analyses have also been made of other ingredients, and show good agreement between the intended amounts and the amounts actually present. For example, upon limited specific analysis for the stated metal, it was found:

Alloy No.	Metal	Intended	Actual
8-----	Cobalt.....	40.0	39.8
8-----	Manganese.....	2.0	1.89
9-----	do.....	0.5	0.55
9-----	Beryllium.....	.02-.03	.02
10-----	do.....	.02-.03	.03

These analyses indicate that the proportions present are well within tolerance, and that the varying percentages in Table 1 truly represent the presence of alloys of successively differing percentage of ingredients.

In this Table 1, the tensile and hardness properties are given for each alloy under two conditions: (1) as "cold-rolled" which for these specimen instances represents a reduction of the order of 15:1 to 10:1, starting with hot-rolled stock of about 0.060 to 0.050 inch, which was quench-annealed and then subjected to the cold rolling; and (2) as "aged," which for the specimens set out in Table 1 represents a processing of the stock as outlined above, followed by heating for 5 hours at 900 degrees F.

Comparisons of the properties under these two conditions show the desirable properties of the cold-rolled stock: and also the effective increase in the tensile properties, particularly the proportional limit and the yield strength, resulting from the aging treatment. The hardness is also increased by aging, but this is largely incidental

for many purposes of employment, as it is the improvement in the elastic properties of the alloys which is so important for superior chronometric springs and other articles where the requirements of maintenance of form and strength are so critical that, for several of the alloys, the material would not be superior to steel for chronometric springs, without the aging treatment.

Alloy 6 with "nil" molybdenum is somewhat lower in strength than alloys of equally similar composition otherwise, but containing 6 to 7 percent of molybdenum. Alloy 6 is useful for mechanical springs, for electrical heating grids, for springs in electrical contactors where high temperatures may be encountered, etc.

Alloy 8 with only 0.05 percent carbon, is somewhat lower in tensile properties both as "cold-rolled" and as "aged" than otherwise similar alloys which are higher in carbon, with alloy 1 as a comparative example. This alloy 8 has a somewhat higher ductility than alloy 1, and is somewhat more readily cold-rolled. Hence, it is useful in preparing parts and cutting instruments which must be capable of withstanding elevated temperatures and which must be formed into shapes including relatively sharp bends.

The data in Table 1 indicate that changes in proportion of the alloy composition can be made without departing from the invention, and that different compositions may be desirable for different applications, or selectively employed for similar applications when different demands for properties may predominate as to importance. It will be noted that the "aged" alloys all show a yield strength (0.02 percent offset) in excess of 200,000 p. s. i., an ultimate tensile strength in excess of 300,000 p. s. i., a modulus of elasticity in excess of 28,800,000 p. s. i., and a hardness (Vickers) in excess of 480, indicating that they are adapted for the critical requirements of chronometric springs.

The alloy of this invention is melted and cast by conventional methods but is preferably produced in a high-frequency induction furnace, cast into slabs or ingots which are first forged and then hot rolled to certain preferred thicknesses, after which the strip is quench annealed by heating at temperatures of 2000 to 2200 degrees F. to effect a solution of the secondary phase or phases thereby decreasing the hardness of the quench-annealed stock. This process is referred to as quench annealing as is the practice in the industry, and the alloy as quench annealed will have a hardness of the order of 250 Brinell or the equivalent. Thicknesses of 0.040 to 0.060 inch have been found satisfactory as the final hot-rolled stock, which is then quench annealed. In commercial practice, the hot reduction can be terminated at 0.200 to 0.250 inch, and then cold-rolling effected down to 0.040 to 0.060 inch, with intervening solution annealing as the hardness becomes too great for practical further reduction. After the final quench annealing, the alloy is cold rolled with at least about 70 percent reduction. It has been found feasible to cold roll the alloys of preferred composition from thicknesses of the order of 0.040 to 0.060 inch down to thicknesses required for watch mainsprings, for example, 0.0044 and 0.004 inch, and stock of only 0.003 inch thickness has been produced. It has been found feasible to make this entire reduction without any intermediate anneal, so that reductions over 90 percent or extensions of over 1000 percent have been effected.

The cold working materially increases the strength of the alloy and refines the grain structure. However, the cold-worked alloy does not have the high strength properties, such as proportional limit, yield strength, and modulus of elasticity required for watch mainsprings. For example, in the cold-worked condition the proportional limit of one specific alloy is likely to be in the range of 130,000 to 160,000 p. s. i., the yield strength (A. S. T. M. method: offset 0.02%) in the range of 160,000 to 180,000 p. s. i. and the modulus of elasticity in the range of about 22,000,000 to 27,000,000 p. s. i. On the other hand, when the alloy has been subjected to a quench anneal, cold rolled, and then age hardened, for example, by heating 5 hours at 900 degrees F. the proportional limit will be of the order of about 200,000 to 240,000 p. s. i., the ultimate strength 340,000 to 380,000 p. s. i., and the yield strength about 250,000 to 290,000 p. s. i. The modulus of elasticity will be close to 30,000,000 p. s. i., and sometimes exceeds that value.

It will be obvious from the foregoing description of the processing of the alloy of this invention that it is not necessary to harden it by quenching the final spring as is the case with the steel springs, but the alloy is cold worked to develop relatively high-strength values and then subjected to an aging treatment at 500 to 1200 degrees F., which further increases the strength values, particularly the proportional limit and the yield strength; for example, an aging treatment of 5 hours at 900 degrees F. may increase the proportional limit by 90 percent or more, and the yield strength by 70 to 80 percent. These are the properties which are considered essential for an article of high elastic properties, which is to stand up in service over long periods of time without taking a set or showing creep.

The resistance of the alloy of this invention to corrosion has been demonstrated by placing an article made of this alloy in a desiccator jar containing water so that it is subjected to a moisture-saturated atmosphere. For comparison purposes, steel springs of the type now generally used in watches were subjected to the same test. All of the steel mainsprings, representative of the existing art, failed by corrosion attack within 48 hours. On the other hand, the articles made of the alloy of this invention were subjected to the test for periods of 3 to 6 months; none of them failed under the rated load, and there was no sign of corrosion.

The ability of the alloy of this invention to resist "set" or "creep" can be determined by installing mainsprings made therefrom in watches, operating them over extended periods of time, and then removing the springs and noting if they returned to their original free-coil position. Commercial steel springs were tested under identical conditions. It is the experience of the watch industry that in such tests, steel springs always show some set even when the service time is only a few days. In fact, watches equipped with steel mainsprings frequently have to have their springs replaced before they leave the factory, because so much set has developed that the spring has lost torque and the watch cannot be adjusted to keep the correct time. In contrast to this behavior, mainsprings of the alloy of this invention showed no loss of torque after having been in service over test periods of 3 and 6 months. Thus, by using an alloy of high elastic properties, set or creep was eliminated; and once the watch was adjusted, it continued to be a good timekeeper.

Thus, by the properties developed in the alloy of this invention, namely, high mechanical properties and resistance to corrosion, a superior alloy for watch mainsprings and other employments requiring high elastic properties and freedom from corrosion, has obviously been produced.

While a major objective of developing this alloy was to find a superior watch mainspring alloy, it has been found that the alloy has other useful applications. For example, it can be used where strength and long life are required at high operating temperatures, such as electrical resistor heating elements, springs for mechanical uses, instruments requiring flame sterilization, pressure conduits and vessels, etc. Electrical resistivity tests on three alloys within the composition range disclosed gave resistivities of 626, 666, and 686 ohms per circular mil foot at room temperature. Some of these resistivities are higher than those found for alloys which are now used for heating elements. For example, under the same conditions, a well-known nickel-chromium alloy showed a resistivity of 650 ohms per circular mil foot. Tests on the alloys as electrical resistor heating elements indicate relatively long life at temperatures up to and including 1800 degrees F.

Still other applications of an alloy of this type have been noted, one of which is for springs to operate at elevated temperatures. Since this alloy age hardens at 500 to 1200 degrees F. and continues to increase in hardness and strength on increase of time of exposure at 900 degrees F., for example, up to at least 5 hours, it is evident that the alloy will not lose its ability to function as a spring material up to about this range of temperatures.

Still other applications of the alloy include instruments and the like requiring keen cutting edges, examples of which are razor blades and surgical instruments. Again the alloy meets the requirements for these applications by its high hardness and strength which enable it to be sharpened to a keen cutting edge and to retain that edge in service. It, furthermore, has the advantage that it is corrosion resistant even at elevated temperatures and, therefore, is not corroded and tarnished by coming in contact with atmospheres or other media which would rust steel.

Having thus described our invention, what we claim is:

1. An alloy consisting essentially of carbon up

to 0.30%, beryllium from 0.01 to 0.09%, manganese up to 3.0%, nickel from 5 to 30%, iron up to 18%, with the sum of the nickel, iron, and manganese being 20 to 50%, and the remainder cobalt, chromium, and molybdenum, with the cobalt from 20 to 50%, the chromium 15 to 30%, and the molybdenum 1 to 10%, and the sum of the chromium and molybdenum being 21 to 37%, said alloy having in solution-annealed condition a hardness below 300 (Vickers).

2. An alloy consisting essentially of carbon from 0.05 to 0.25%, beryllium from 0.01 to 0.09%, manganese from 0.5 to 3.0%, with the sum of the nickel and iron being 25 to 42%, with the nickel from 15 to 30%, and the iron up to 15%, and the remainder cobalt, chromium, and molybdenum, with the cobalt from 28 to 45%, the chromium from 15 to 30%, the molybdenum from 3 to 10%, with the sum of the chromium and molybdenum being 24 to 35%, said alloy having in solution-annealed condition a hardness below 300 (Vickers).

3. An alloy consisting essentially of carbon from 0.10 to 0.20%, beryllium from 0.01 to 0.09%, manganese 2%, nickel 15.5%, iron 15%, cobalt 40%, chromium 20%, and molybdenum 7%: said alloy having in solution-annealed condition a hardness below 300 (Vickers).

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