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3,307,939

CORROSION-RESISTING COBALT-CHROMIUM-TUNGSTEN ALLOYS

Anton Bäumel, Lank (Lower Rhine) Germany, assignor to Gebr. Bohler & Co. Aktiengesellschaft, Vienna, Austria

No Drawing. Filed June 2, 1964, Ser. No. 372,089

Claims priority, application Austria, June 4, 1963,

A 4,457/63

2 Claims. (Cl. 75-134)

Cobalt-chromium-tungsten alloys having a high abrasion resistance and high-temperature stability and containing a relatively large amount of carbon consist in the as-cast and as-welded conditions substantially of a large amount of hard chromium-tungsten carbides, which are embedded in a non-transforming, cubic face-centered, tough cobalt-chromium matrix. The cooperation of the hard carbides and the tough matrix is responsible for the high abrasion resistance and high-temperature stability of these alloys. The two main constituents of the structure are also decisive for the corrosion behavior. Whereas the carbides are hardly susceptible to hydrochloric acid and sulfuric acid, these acids attack the cobalt-chromium matrix. As the matrix is dissolved out of the structure, the carbide lattice loses its coherence and can readily be detached by mechanical means from the core which has not yet been attacked. Hence, the resistance to corrosion can be improved only by an improvement of the resistance of the matrix in which the carbides are embedded.

The present invention provides cobalt-chromium-tungsten alloys which contain additions of copper and, if desired, molybdenum, for a substantially increased resistance to corrosion. Two alloys having the following composition have been prepared by melting:

TABLE 1.—CHEMICAL COMPOSITION OF COBALT-CHROMIUM-TUNGSTEN ALLOYS WITHOUT AND WITH COPPER AND MOLYBDENUM

Alloy Number	C	Si	Mn	Cr	W	Co <sup>1</sup>	Mo	Cu	Fe
1-----	2.2	0.15	0.22	30.3	20.3	38.4	-----	-----	8.8
2-----	2.2	0.17	0.17	30.3	19.0	40.9	3.0	2.0	2.3

<sup>1</sup> Calculated as the balance.

It is apparent from Table 2 that the resistance to corrosion is much improved by the addition of copper and molybdenum.

TABLE 4.—WEIGHT LOSS OF THE COBALT-CHROMIUM-TUNGSTEN ALLOYS OF TABLE 3, IN AS-CAST AND AS-WELDED CONDITION, IN HYDROCHLORIC ACID AND SULFURIC ACID, IN GRAMS PER SQUARE METER PER HOUR

Alloy Number	Content		10-percent hydrochloric acid				20-percent sulfuric acid			
	Mo	Cu	Room temperature		Boiling temperature		Room temperature		Boiling temperature	
			As-cast	As-welded	As-cast	As-welded	As-cast	As-welded	As-cast	As-welded
3-----	-----	3.5	0.6	0.9	258	255	0.08	1.5	7.6	1.7
4-----	3.4	2.3	1.2	0.8	234	267	0.02	0.03	6.0	2.4
5-----	3.1	4.1	0.7	0.7	211	310	0.13	0.2	2.2	9.4
6-----	4.8	5.5	1.4	0.9	212	234	0.02	0.4	4.7	5.3
7-----	6.7	3.4	3.2	0.7	207	229	0.04	0.3	3.8	4.2

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TABLE 2.—WEIGHT LOSS OF THE COBALT-CHROMIUM-TUNGSTEN ALLOYS OF TABLE 1 IN HYDROCHLORIC AND SULFURIC ACIDS, IN GRAMS PER SQUARE METER PER HOUR

Alloy Number	10 percent hydrochloric acid		20 percent sulfuric acid	
	Room temperature	Boiling temperature	Room temperature	Boiling temperature
1-----	6	1,120	5.2	430
2-----	0.9	250	1.0	4.3

The weight losses of the alloy which contains molybdenum and copper are at room temperature about one fifth of those of the alloy which does not contain molybdenum and copper. The test in boiling sulfuric acid shows particularly that the weight loss is reduced to about one hundredth by the joint presence of copper and molybdenum. The improved corrosion behavior due to copper and molybdenum has been confirmed by electrochemical measurements carried out on these alloys in 1N sulfuric acid at room temperature.

To find out whether a further increase in the resistance to corrosion can be achieved by larger additions of copper and molybdenum, a number of alloys having the composition indicated in Table 3 were prepared by melting.

TABLE 3.—CHEMICAL COMPOSITION OF COBALT-CHROMIUM-TUNGSTEN ALLOYS CONTAINING COPPER AND MOLYBDENUM

Alloy Number	C	Si	Mn	Cr	W	Co <sup>1</sup>	Mo	Cu	Fe
3-----	2.5	0.54	0.27	31.9	13.4	46.4	-----	3.5	1.5
4-----	2.3	0.55	0.33	31.0	18.8	41.4	3.4	2.3	0.0
5-----	2.5	0.47	0.24	31.6	13.0	42.9	3.1	4.1	2.1
6-----	2.3	0.49	0.25	31.7	13.3	39.8	4.8	5.5	1.9
7-----	2.3	0.49	0.26	31.7	14.0	39.8	6.7	3.4	1.4

<sup>1</sup> Calculated as the balance.

For a greater latitude regarding the addition of copper and molybdenum, the tungsten content of these melts was reduced to about 13%, compared to 20% in the alloys of Table 1. The cobalt content in the alloys was calculated to avoid a substantial increase of the iron content above 2%.

Table 4 shows the weight losses of the alloys of Table 3 in 10% hydrochloric acid and 20% sulfuric acid at room temperature and boiling temperature.

These alloys were tested for weight losses in the form of welding rods and of samples of welds made from such rods. Table 5 indicates the weight losses of samples of welds of conventional cobalt-chromium-tungsten alloys under corresponding conditions. A comparison of the weight losses indicated in Tables 4 and 5 shows the superiority of the alloys which contain copper, or copper and molybdenum, over the conventional alloys.

the fine structure show that the addition of copper and molybdenum does not appreciably affect the amount and nature of the precipitated carbides. The added copper and molybdenum are enriched mainly in the matrix to improve its resistance to corrosion.

An adverse effect of copper and molybdenum on the abrasion resistance and high-temperature stability is not to be expected. The Rockwell C hardness numbers of the

TABLE 5.—CHEMICAL COMPOSITION AND WEIGHT LOSS IN GRAMS PER SQUARE METER PER HOUR IN HYDROCHLORIC ACID AND SULFURIC ACID OF CONVENTIONAL COBALT-CHROMIUM-TUNGSTEN ALLOYS IN AS-WELDED CONDITION

Percentage content of—									10% Hydrochloric acid		20% Sulfuric acid	
C	Si	Mn	Cr	W	Co <sup>1</sup>	B	Nb	Fe	Room temp.	Boiling temp.	Room temp.	Boiling temp.
1.74	2.57	0.1	27.9	5.6	31.8	-----	-----	30.3	33.5	2,900	71.0	113
2.15	0.65	0.04	24.6	13.5	58.5	-----	-----	0.6	4.3	1,231	12.8	178
2.62	0.34	0.04	31.1	18.5	46.5	-----	-----	0.9	3.7	1,411	20.0	146
1.37	0.8	0.1	24.3	4.6	67.9	-----	-----	0.9	3.5	861	18.2	188
2.4	0.5	0.12	29.0	19.0	43.0	0.65	2.5	<2.0	2.9	1,352	16.3	188

<sup>1</sup> Calculated as the balance.

It is also apparent from Table 4 that alloys 6 and 7 having the highest contents of copper and molybdenum do not have a higher resistance than the alloys 4 and 5 having lower contents of these elements. It is believed that the optimum composition of a cobalt-chromium-tungsten alloy having a high wear resistance and an increased resistance to corrosion, particularly by sulfuric acid and similar media which do not have a very strong reducing action, is within the following limits:

2.2–2.5% C, 30–32% Cr, 13–20% W, 39–47% Co, up to 1% Mn, up to 1% Si, 0.3–6% Cu, and, if desired, up to 6% Mo.

The following alloy composition has proved particularly favorable:

2.2% C,  $\leq 1\%$  Si,  $\leq 1\%$  Mn, 30% Cr, 14% W, 46% Co, 4% Mo, 2% Cu.

By the attack of acids on the alloys, the matrix is dissolved out first so that the carbide remains on the sample as a relatively firmly adhering covering. This covering is scraped from the workpiece when the same is subjected to corrosion and abrasion at the same time. For this reason the carbide covering which can be mechanically removed must also be considered when determining the weight loss. For this reason, the carbide residue has always been removed with a steel wire brush before the weight loss was determined. The resulting weight losses are higher than those obtained when the carbide covering is left on the samples.

The isolation of the residue and X-ray examinations of

alloys indicated in Table 3 are between 52 and 60 and increase with increasing contents of copper and molybdenum.

It is also known that the high-temperature hardness of cobalt-chromium-tungsten alloys is improved by an addition of molybdenum up to 4% so that molybdenum results in an improvement of two important properties of the alloy.

What is claimed is:

1. A corrosion-resisting cobalt-chromium-tungsten alloy consisting essentially of 2.2–2.5% carbon, 30–32% chromium, 13–20% tungsten, 39–47% cobalt, up to 1% manganese, up to 1% silicon, 0.3–6% copper and up to 6% molybdenum.

2. A corrosion-resisting cobalt-chromium-tungsten alloy consisting essentially of 2.2% carbon, 30% chromium, 14% tungsten, 46% cobalt, 4% molybdenum, 2% copper, up to 1% manganese, and up to 1% silicon.

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DAVID L. RECK, *Primary Examiner*.

R. O. DEAN, *Assistant Examiner*.