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HOT ROLLED METAL ARTICLE AND METHOD OF MAKING SAME

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This invention relates to hot rolled articles such as tubes, plates, sheets, strips, rods, of low carbon austenitic ferrous chromium-nickel alloys containing molybdenum, and to methods of making the same.

Austenitic ferrous chromium-nickel alloys, and especially the largely used 18–8 alloy, are well known and have been used in industry for several years where high resistance to corrosion and oxidation at high temperatures and strength at high temperatures is required. Such alloys are available in various commercial forms, such as sheet, plate, wire, rods, tubes, etc. For some purposes, however, the corrosion resistance of the usual chromium-nickel alloy steels has not been found sufficient, especially in cases where the metal is subjected to hot sulfurous acid under pressure or to hot acetic acid. Corrosion resistance under such conditions has been improved by the addition to these alloys of molybdenum, usually in amounts of 2 to 4%. The molybdenum, in addition to increasing corrosion resistance, also imparts red hardness and adds to the high temperature strength of the alloy. Such molybdenum-containing high chromium-nickel alloys have usually had from .1 to 4% of carbon, but it is desirable that the carbon content of these alloys be kept low in order to increase the corrosion resistance and reduce tendency to inter-granular corrosion.

Great difficulty has been experienced in hot working low carbon austenitic molybdenum-containing alloys to produce plates, sheets, strips, rods, etc., and it has not been found possible prior to the present invention to produce commercially hot-pierced seamless tubes of these alloys. When it is attempted to pierce in a cross-rolling mill billets of low carbon austenitic chromium-nickel alloys containing a substantial amount of molybdenum, for example, an alloy of .05–.10% carbon, 18% chromium, 8.5% nickel, and 3% molybdenum, the metal tears, checks and breaks apart so that it has been found impossible to produce satisfactory useful tubes. While the defects developed in hot rolling these alloys are not so great as in the production of tubes, yet the hot shortness of the alloys and resulting tendency to crack or tear and to develop surface defects makes it very difficult and expensive to produce salable hot-rolled articles.

The increased hardness and strength of the alloys due to the contained molybdenum make them more difficult to work hot than alloys without molybdenum but otherwise similar, but this greater hardness and strength is not the cause of the extreme difficulty of hot working and of the failures of attempts to make seamless tubes of these alloys. Increased hardness and strength can be offset by using more power for piercing and for other hot rolling.

We have discovered that the hot shortness which causes the metal of the heated billet to tear and check and crack in the piercing mill and which makes it difficult to produce other hot rolled articles is due to the formation of delta iron in the heated alloy caused by the molybdenum together with the low carbon. Apparently the delta iron solid solution of chromium, nickel, carbon and molybdenum has different mechanical properties at the elevated working temperatures and is weaker than the austenitic base structure, and this causes hot shortness which results in shearing, tearing or otherwise rupturing along the weaker delta areas. We have found that even a small amount of the delta constituent will cause great difficulty and disastrous results when it is attempted to pierce billets of these alloys.

Chromium and molybdenum promote, and nickel and carbon lessen, the formation of delta iron in the austenitic chromium-nickel stainless steels. We have found that by suitably controlling the ratio of nickel to chromium plus molybdenum the presence of delta iron can be eliminated even in very low carbon austenitic alloys, and that billets made of the resulting alloys can readily be pierced and reduced, producing entirely satisfactory tubes free from tears, cracks, or other defects. Such delta-iron-free alloys are homogeneous single-phase alloys composed solely of austenitic structure, and having working characteristics distinct from previously known alloys.

Silicon also promotes the formation of delta iron, and manganese hinders its formation, but the effect of the small quantities of these elements normally present in these alloys can be neglected, especially as they act in opposite directions and so tend to neutralize each other.

The carbon content of alloys for making tubes according to the invention should not exceed about 0.15%, and is desirably less than 0.12% and may be extremely low. Molybdenum for the desired corrosion resistance and heat strength should not be less than 1% or more than 4% and more generally between 1.5% and 3%. Chromium should be not less than about 14% and not more than about 20%, and the combined chromium plus twice the molybdenum should not exceed 25% of the whole. Nickel should be between about

9% and about 18%. The amount of nickel required to give the desired single phase austenitic structure at the elevated working temperatures depends, as we have found, on the sum of the chromium content plus twice the molybdenum content, and we have found that the amount of nickel required for this result should be in excess of the amount required by the formula $12(x-8)=(y-16)^2$, where x is the nickel content and y is the sum of the chromium content plus twice the molybdenum when the carbon is about 0.10%. If the carbon is less than about 0.10% the amount of nickel required will be greater than that called for by the formula, and when the carbon is more than about 0.10% the amount of nickel required will be less than called for by the formula, in either case in about the proportion of 30 for nickel to 1 for carbon. The alloy may contain the usual minor elements, but silicon should not exceed .75% and is most desirably below this amount.

Most desirably, the alloys are within the following ranges:

	Percent
Carbon	0.03 to 0.12
Chromium	14 to 19
Molybdenum	1.5 to 3
Nickel	10 to 16

The higher the chromium and molybdenum content within the given range, the higher also should be the nickel content in accordance with the formula.

The following are examples of compositions suitable for producing tubes within the invention:

	#1	#2	#3	#4	#5
Carbon	.138	.11	.09	.15	.06
Manganese	.45	.45	.40	.40	.50
Silicon	.35	.42	.12	.35	.30
Chromium	16.56	15.36	13.92	18.25	18.40
Nickel	13.09	12.69	12.89	15.00	14.87
Molybdenum	3.00	2.10	2.38	3.00	1.50

Billets, or rounds, for conversion into tubes are made from the alloy by forging and rolling cast ingots of the alloy or in any other suitable manner. In converting the billets into tubes they are heated to proper piercing temperature in the neighborhood of 2100° F. and then passed through a cross-rolling piercing mill to produce comparatively thick-walled tubes or hollows, the wall thickness of which may then be reduced in any usual or suitable manner. In making other hot-rolled articles according to the invention, such as plates, sheets, strips, rods, etc., the alloy is cast to form suitable ingots which are forged or rolled to form blooms or slabs, according to the articles to be produced, and such blooms or slabs are then hot-rolled to form the desired articles.

The usual starting temperature for hot-rolling articles of the kind to which this invention relates is in the neighborhood of 2200° F. The expression "hot-rolled articles" as used in claims 2, 5, 6 and 8 is, therefore, to be understood as meaning that the metal has been rolled while heated to a temperature which at the start of the rolling is substantially above 1800° F.

What is claimed is:

1. A hot-pierced seamless tube made of a low carbon austenitic ferrous chromium-nickel-molybdenum alloy containing 14 to 20 percent chromium, 1 to 4 per cent molybdenum, 9 to 18 percent nickel, and not over about 0.15 percent carbon, the amount of nickel within the stated range being sufficient to prevent formation of delta iron when the alloy is heated to piercing temperature.

2. A hot-rolled article made of a low carbon austenitic ferrous chromium-nickel-molybdenum alloy containing 14 to 20 percent chromium, 1 to 4 percent molybdenum, 9 to 18 percent nickel, and not over about 0.15 percent carbon, the sum of the chromium and twice the molybdenum not exceeding 25%, and the amount of nickel within the stated range being sufficient to prevent formation of delta iron when the alloy is heated to hot-rolling temperature.

3. A hot-pierced seamless tube made of a low carbon austenitic ferrous chromium-nickel-molybdenum alloy containing 14 to 20 percent chromium, 1 to 4 percent molybdenum, 9 to 18 percent nickel, and not more than 0.15 percent carbon, the sum of the chromium and twice the molybdenum not exceeding 25 percent, and the nickel being in excess of the amount required by the formula $12(x-8)=(y-16)^2$, where x is the nickel content and y is the sum of the chromium plus twice the molybdenum when the carbon is about 0.10 percent, the minimum for the nickel being greater than required by the formula when the carbon is less than 0.10 percent and being less than required by the formula when the carbon is more than about 0.10 percent in about the proportion of 30 to 1.

4. A hot-pierced seamless tube made of an austenitic alloy as in claim 3, in which the chromium is between 14 and 19 percent, the molybdenum between 1.5 and 3 percent, the nickel between 10 and 16 percent, and the carbon not over about 0.12 percent.

5. A hot-rolled article made of a low carbon austenitic ferrous chromium-nickel-molybdenum alloy containing 14 to 20 percent chromium, 1 to 4 percent molybdenum, 9 to 18 percent nickel, and not more than 0.15 percent carbon, the sum of the chromium and twice the molybdenum not exceeding 25 percent, and the nickel being in excess of the amount required by the formula $12(x-8)=(y-16)^2$, where x is the nickel content and y is the sum of the chromium plus twice the molybdenum when the carbon is about 0.10 percent, the minimum for the nickel being greater than required by the formula when the carbon is less than 0.10 percent and being less than required by the formula when the carbon is more than about 0.10 percent in about the proportion of 30 to 1.

6. A hot-rolled article made of an austenitic alloy as in claim 5, in which the chromium is between 14 and 19 percent, the molybdenum between 1.5 and 3 percent, the nickel between 10 and 16 percent, and the carbon not over about 0.12 percent.

7. The method of making seamless tubes, which comprises forming a billet of an austenitic alloy containing 14 to 20 percent chromium, 1 to 4 percent molybdenum, 9 to 18 percent nickel, and not more than about 0.15 percent carbon, the sum of the chromium and twice the molybdenum not exceeding 25 percent, and the nickel being in excess of the amount required by the formula $12(x-8)=(y-16)^2$ where x is the nickel content and y is the sum of the chromium plus twice the molybdenum when the carbon is about 0.10 percent, the minimum for the nickel being greater than required by the formula when the carbon is less than 0.10 percent and being less than required by the formula when the carbon is more than about 0.10 percent in about the

proportion of 30 to 1, heating the billet to piercing temperature, and then cross-rolling and piercing the hot billet to form a tube.

8. The method of making hot-rolled articles, which comprises casting an ingot of an austenitic alloy containing 14 to 20 percent chromium, 1 to 4 percent molybdenum, 9 to 18 percent nickel, and not more than about 0.15 percent carbon, the sum of the chromium and twice the molybdenum not exceeding 25 percent and the nickel being in excess of the amount required by the formula $12(x-8)=(y-16)^2$ where x is the nickel content and y is the sum of the chromium plus twice the molybdenum when the carbon is about 0.10 percent, the minimum for the nickel being greater than required by the formula when the carbon is less than 0.10 percent, and being less than required by the formula when the carbon is more than about 0.10 percent in about the proportion of 30 to 1, forging the ingot to form a body of the desired shape for rolling, and hot-rolling said body to form the desired article.

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