United States Patent Office 3,162,530 Patented Dec. 22, 1964

3,162,530

FABRICATION OF Cr-Y SHEET

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No Drawing. Filed Feb. 12, 1963, Ser. No. 257,840
9 Claims. (Cl. 75—214)

This invention relates to high-temperature, oxidation-resistant alloys and more specifically to a chromium-yttrium alloy and an improved method for making the same.

Prior to this invention chromium-yttrium was known to be a good high-temperature, oxidation-resistant alloy. Since the maximum solubility of yttrium in chromium is not much over 1%, the alloy most commonly used was Cr-1 w/o Y (1 percent Y by weight—balance chromium). This alloy, as heretofore prepared by melting techniques, was sufficiently ductile to permit the formation of structural shapes by usual metal working methods but was not ductile enough to permit the formation of thin sheets and would not permit the formation of parts by stamping. Further, this alloy as previously prepared by powder metallurgy fell far short of having the maximum possible theoretical density of 7.16 g./cc.

Chromium-1 w/o Y is very susceptible to crack propagation. Such materials are more easily fabricated when the grain size is small and percent of theoretical density is at the maximum. Arm melting leads to completely dense material; however, the resulting grain size is very large (greater than ASTM 1). Powder metallurgy leads to a fine grain size but heretofore maximum density Cr-1 w/o Y was unattainable.

It is therefore an object of this invention to produce a Cr-1 w/o Y alloy having the maximum theoretical density by the powder metallurgy approach with a fine grain zize (less than ASTM 7).

Nitrogen contamination has been shown by previous investigations to be very detrimental to the ductility of Cr-1 w/o Y by raising the brittle-to-ductile transformation temperature. By keeping the nitrogen content as low as possible, preferably under 100 p.p.m. (parts per million), a ductile material can be produced that can be rolled to sheet. It is therefore another object of this invention to provide a process by which high purity can be maintained from the starting powders to the finished product, namely 8 mil Cr-1 w/o Y sheet.

Due to its high vapor pressure, chromium and its alloys, such as Cr-1 w/o Y, cannot be sintered at high temperatures and high vacuum (5×10^{-6} mm. Hg). Sintering in pure hydrogen at high temperatures is a better technique for pure chromium; however, this technique is not applicable to the Cr-1 w/o Y alloy since the yttrium will hydride. Previous investigations employing a one-step high temperature sintering treatment for the densification were unsuccessful in achieving maximum density.

It is therefore a principal object of this invention to provide a two-step sintering process to achieve maximum density pure Cr-1 w/o Y compacts for rolling to 8 mil stampable sheet.

In the first step the yttrium is put into solution in the chromium and sintering is initiated. The compact is cold coined at high pressure after the solution treatment to a higher density. This density increase would be impossible if the yttrium is hydrided or the chromium is contaminated. The use of high pressure also imparts a high degree of cold work to the compact which accelerates sintering and thereby results in complete densification in the second step. As a result of the first step the Cr-1 w/o Y compact can be heated for a long time in hydrogen, thereby preventing vaporization of the chromium and hydriding of the yttrium.

In making the improved alloy, high purity chromium powder (nitrogen less than 20 p.p.m.), either —200 mesh Lunex or —270 Cooper, is blended with —325 Michigan Chemical yttrium powder. This blending is done under argon for 20 hours. Compacts, 1" diameter x 3" length, are made without exposure to air by pressing at 50 t.s.i. in a sealed die. Exposure to air is avoided by providing an argon atmosphere in the die. Sintering is next performed and, in accordance with this invention, it is performed in two distinct steps.

In the first step the compact is heated to 2700° F. in a vacum of 5×10^{-6} mm. of Hg for ½ hour. Heating is then continued for 1½ hours in a ⅓ atmosphere of pure hydrogen which can be made from the decomposition of yttrium hydride. By heating the compact in vacuum prior to introducing the hydrogen, yttrium will go into solution without the formation of yttrium hydride. Densities at this point in the process measure 85% of theoretical. Cold coining at 60 t.s.i. brings the density of the compact up to 93% of theoretical.

In the second sintering step the coined compact is heated for 5 hours in pure hydrogen at 2700° F. Following this second step the density ranges from 98–100% of theoretical density. Nitrogen content at this point is less than 40 p.p.m.

Dense compacts are then sealed in evacuated pure nickel cans at 5×10^{-5} mm. of Hg. By press forging at 400 t.s.i. at 2350° F., a ¼" thick asembly is obtained having a cross section of nickel-Cr-1 w/o nickel. The assembly is next hot rolled at 2200° F. to 36 mils and then further rolled at 1800° F. to 9 mils. The nickel sheet is then removed by pickling in nitric acid. Nitrogen content of the Cr-1 w/o Y at this point is less than 80 p.p.m. As well as protecting the Cr-1 w/o Y from contamination during rolling, the use of pure nickel as a sheath material gives a better surface finish to the Cr-1 w/o Y sheet than other less oxidation-resistant materials and still allows removal by pickling in nitric acid which will not attack the Cr-1 w/o Y sheet. To further improve the appearance of the Cr-1 w/o Y sheet, an electrolytic polish in hydrochloric acid can be used.

In practicing this invention, I use this final step of subjecting the Cr-1 w/o Y sheet to a final pickling in hydrochloric acid to remove about 1 mil of the sheet following the removal of the nickel can because it considerably improves the ductility of the Cr-1 w/o Y. This step is particularly recommended if stamping operations are to be subsequently performed on the sheet. I do not know the reason for this increase in ductility and stampability but it is quite pronounced and cannot be attributed to the mere reduction in thickness of the sheet. Attempts to roll Cr-1 w/o Y without the nickel sheath have not, however, been successful.

Before removal of the nickel sheath, the 8 mil sheet can be cut with a shears without cracking. Also, for the first time such a sheet has been provided from which stamped extended surfaces, such as fins for heat exchangers and the like, is entirely possible.

Stamping of the Cr-1 w/o Y sheet at room temperature is possible for many operations, while other more difficult stamping operations may advantageously be performed at 800° F. Testing has shown that sheet material formed by this process retains maximum ductility down to 500° F.

It will thus be evident that by this invention a new process has been provided for producing Cr-1 w/o Y sheet and that the sheet produced has not only the maximum theoretical density but also has such improved ductility as to permit 8 mil stampable sheet to be rolled from it.

What it is desired to claim is:

1. A binary sintered alloy of chromium-yttrium consist-

ing of Cr-1 w/o Y having less than 100 p.p.m. nitrogen and having a density of approximately 100% of theoretical maximum density and having extreme ductility enabling sheath rolling into a stampable 8 mil sheet.

2. A stampable sheet of sintered chromium-yttrium alloy consisting of Cr-1 w/o Y having less than 100 p.p.m. nitrogen and having a density approaching the maximum theoretical density of 7.16 g./cc. and having a grain size less than ASTM 7.

3. A ductile sintered alloy of chromium-yttrium consisting of Cr-1 w/o Y having less than 100 p.p.m. nitrogen and having a density of approximately 7.16 g./cc. and a grain size less than ASTM 7.

4. A method for producing a dense and ductile Cr-1 w/o Y sheet by powder metallurgy which comprises, blending under argon fine chromium and yttrium powders having nitrogen less than 20 p.p.m., pressing the blended powders into a compact, putting the yttrium into solution in the chromium without yttrium hydride formation by heating the compact to 2700° F. in a vacuum of 5×10^{-6} mm. of Hg for ½ hour, then introducing ⅓ atmosphere of pure hydrogen and continuing heating for 1½ hours, cold coining the compact at 60 t.s.i., sintering for 5 hours in pure hydrogen at 2700° F., sealing the compact in a nickel can at 5×10^{-5} mm. of Hg, press forging the assembly at 400 t.s.i. at 2350° F., hot rolling the assembly at 2200° F. to approximately 36 mils, continuing rolling at 1800° F. to approximately 9 mils, and pickling in nitric acid to remove the nickel sheath.

5. A method for producing a dense and ductile Cr-1 w/o Y sheet by powder metallurgy which comprises, blending under argon fine chromium and yttrium powders having nitrogen less than 20 p.p.m., pressing the blended powders into a compact, putting the yttrium into solution in the chromium without yttrium hydride formation by heating the compact to 2700° F. in a vacuum of 5×10^{-6} mm. of Hg for ½ hour, then introducing ⅓ atmosphere of pure hydrogen and continuing heating for 1½ hours, cold coining the compact at 60 t.s.i., sintering the compact for 5 hours in pure hydrogen at 2700° F., sealing the compact in a nickel can at 5×10^{-5} mm. of Hg, press forging the assembly at 400 t.s.i. at 2350° F., hot rolling the assembly at 2200° F. to approximately 36 mils, continuing rolling at 1800° F. to approximately 9 mils, removing the nickel sheath by pickling in nitric acid, and pickling the Cr-1 w/o Y sheet in hydrochloric acid to remove a small amount of the surface of the sheet.

6. A method for producing an 8 mil Cr-1 w/o Y sheet by powder metallurgy which comprises, blending under an inert gas chromium and yttrium powders containing less than 100 p.p.m. of nitrogen, pressing the powders into a compact, putting the yttrium into solution in the chromium without yttrium hydride formation by heating the compact to 2700° F. in a vacuum of 5×10^{-6} mm. of Hg for ½ hour, introducing ⅓ atmosphere of pure hydrogen and continuing heating for 1½ hours, and cold coining the compact at 60 t.s.i., sintering for 5 hours in pure hydrogen at 2700° F., sealing the compact in a nickel can at 5×10^{-5} mm. of Hg, press forging the assembly at 400 t.s.i. at 2350° F., hot rolling the assembly to finished dimensions, and removing the nickel sheath by pickling in nitric acid.

7. A sintering process for converting a Cr-1 w/o Y compact of chromium and yttrium powders into a compact having a density ranging from 98–100% of maximum theoretical density, first putting the yttrium into solution in the chromium without yttrium hydride formation by heating the compact to 2700° F. in a vacuum of 5×10^{-6} mm. of Hg for ½ hour, introducing ⅓ atmosphere of pure hydrogen while continuing the heating for 1½ hours, cold coining at 60 t.s.i. to bring the density up to about 93% of maximum theoretical density, and then heating the coined compact for 5 hours in pure hydrogen at 2700° F. to bring the final density of the compact into the range of 98–100% of theoretical density.

8. A method for producing by powder metallurgy a stampable Cr-1 w/o Y sheet having approximately 100% maximum theoretical density which comprises, blending fine chromium and yttrium powders having nitrogen less than 20 p.p.m. under argon gas for 20 hours, pressing the blended powders into a compact in a die in an argon atmosphere at 50 t.s.i., heating the compact to 2700° F. in a vacuum of 5×10^{-6} mm. of Hg for ½ hour, introducing ⅓ atmosphere of pure hydrogen and continuing heating for 1½ hours, cold coining the compact at 60 t.s.i., heating the compact for 5 hours in pure hydrogen at 2700° F., sealing the compacts in nickel cans at 5×10^{-5} mm. of Hg, press forging at 400 t.s.i. at 2350° F., hot rolling the assembly at 2200° F. to 36 mils, continuing rolling at 1800° F. to approximately 9 mils, and pickling in nitric acid to remove the nickel sheath.

9. A method for producing by powder metallurgy a stampable Cr-1 w/o Y sheet having approximately 100% maximum theoretical density which comprises, blending fine chromium and yttrium powders having nitrogen less than 20 p.p.m. under argon gas for 20 hours, pressing the blended powders into a compact in a die in an argon atmosphere at 50 t.s.i., heating the compact to 2700° F. in a vacuum of 5×10^{-6} mm. of Hg. for ½ hour, introducing ⅓ atmosphere of pure hydrogen and continuing heating for 1½ hours, cold coining the compact at 60 t.s.i., heating the compact for 5 hours in pure hydrogen at 2700° F., sealing the compacts in nickel cans at 5×10^{-5} mm. of Hg, press forging at 400 t.s.i. at 2350° F., hot rolling the assembly at 2200° F. to 36 mils, continuing rolling at 1800° F. to approximately 9 mils, pickling in nitric acid to remove the nickel sheath, and pickling the Cr-1 w/o Y sheet in hydrochloric acid to remove a small amount of the surface of the sheet to further enhance its ductility.

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