

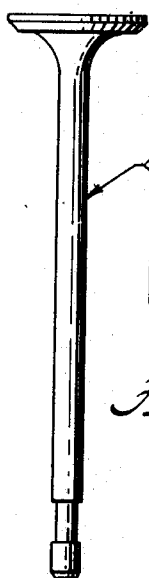
Feb. 24, 1970

R. E. EPPICH

3,497,349

AIR CASTABLE NICKEL ALLOY VALVE

Filed Sept. 19, 1966



0-0.1% CARBON
0-1% SILICON
0-1% MANGANESE
0-10% IRON
15-30% CHROMIUM
4-8.5% NIOBIUM
0-0.1% BORON
0.3-1.7% ATOMIC % { TUNGSTEN
+
MOLYBDENUM
BALANCE - NICKEL

Fig. 1

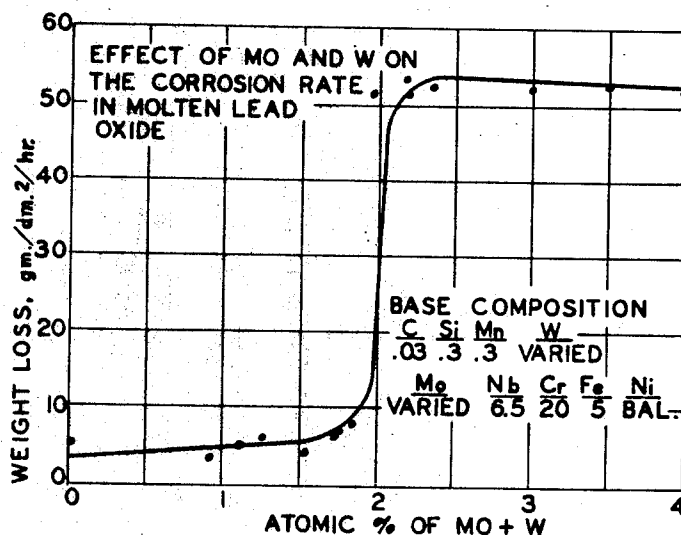


Fig. 2

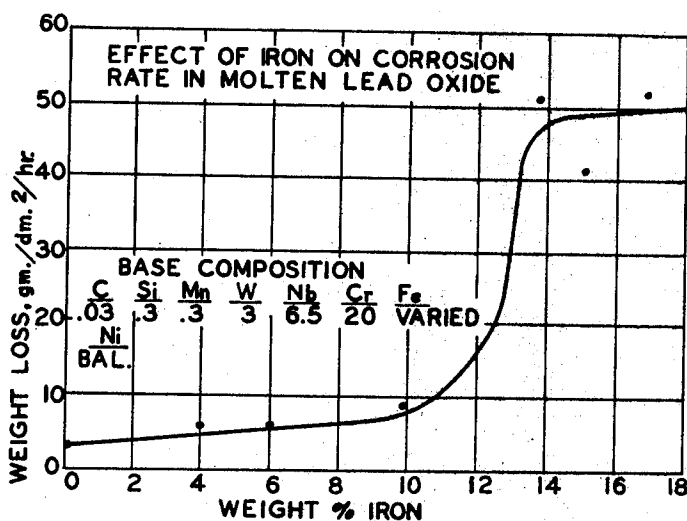


Fig. 3

INVENTOR.
Robert E. Eppich

BY

Peter P. Kozak

ATTORNEY

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3,497,349

AIR CASTABLE NICKEL ALLOY VALVE

Robert E. Eppich, Southfield, Mich., assignor to General Motors Corporation, Detroit, Mich., a corporation of Delaware

Filed Sept. 19, 1966, Ser. No. 580,263

Int. Cl. C22c 19/00; F01I 3/02

U.S. Cl. 75-171

5 Claims

ABSTRACT OF THE DISCLOSURE

An air castable nickel base alloy suitable for automotive exhaust valves is disclosed having exceptional resistance to corrosive attack by the combustion products of leaded internal combustion engine fuels. In a preferred embodiment the alloy consists essentially by weight of 0 to 0.1% carbon, 0 to 10% iron, 15 to 30% chromium, 4 to 8.5% niobium, 0 to about 5% tungsten, 0 to about 2.5% molybdenum, and the balance nickel, the sum of the atomic percentage of tungsten and the atomic percentage of molybdenum in the alloy being in the range of 0.3 to 1.7%.

This invention relates to an air-castable nickel-based alloy and more particularly to a nickel alloy which exhibits a marked resistance to corrosive attack in the presence of the combustion products of leaded diesel and automotive fuels.

Exhaust valves in spark and compression ignited internal combustion engines are subjected to both the relatively high operating temperatures of the combustion chamber and the corrosive reaction products of the fuel combustion. To produce valves capable of standing up under such conditions resort has been made to the use of wrought nickel-based alloys, or austenitic steels which are hard faced with a material having suitable hot strength properties. However, the fabrication of the wrought alloys or the hard faced austenitic steels is an expensive, time consuming process and the art has long searched for a suitable castable exhaust valve alloy. Most known nickel-based alloys which meet the hot strength requirements of exhaust valves must be melted and poured in a vacuum to avoid oxidation of the hardening elements. They cannot be cast in simple inexpensive sand or resin bonded shell molds. Other casting alloys which could be air melted contain substantial amounts of cobalt which is an expensive strategic material.

Recently a nickel-based alloy was developed which can be cast in air and which appears to have sufficient hot strength for use as a heavy duty exhaust valve. This composition is disclosed in United States Patent No. 3,069,258. However, exhaust valves formed of this material tend to corrode when exposed to the combustion products of a leaded internal combustion engine fuel.

Therefore, it is an object of the present invention to provide an air castable nickel-based alloy having high hot strength properties and exhibiting resistance to attack by leaded internal combustion engine fuels.

It is a more specific object of my invention to provide an air-castable nickel-based alloy, which is strength-

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ened by a dispersed phase comprised of tungsten niobide, molybdenum niobide, and nickel niobide of a critical composition which resists attack by molten lead oxide as well as the combustion products of leaded internal combustion engine fuels.

It is a still further object of my invention to provide an exhaust valve, cast from a nickel-based alloy, which is suitable for use in an internal combustion engine of either the compression ignition or spark ignition type in contact with the combustion products of leaded fuels.

These and other objects are accomplished in accordance with my invention by casting a one- or two-piece exhaust valve in a sand mold or resin bonded shell mold from a melt containing by weight 0 to 0.1% carbon, 0 to 10% iron, 15 to 30% chromium, 4 to 8.5% niobium, 0 to about 5% tungsten and 0 to about 2.5% molybdenum, with the further specification that the value of the atomic percentage of tungsten plus the atomic percentage of molybdenum necessarily lie in the range of 0.3 to 1.7%. The balance of the melt composition is substantially all nickel.

Other objects of my invention will become more apparent in view of the following detailed description thereof, reference being made to the attached drawings in which:

FIGURE 1 is a typical exhaust valve, cast from a nickel-based composition in accordance with my invention;

FIGURE 2 is a graph summarizing experiments which illustrate the unexpected criticality of the tungsten plus molybdenum concentrations in my nickel-based alloy;

FIGURE 3 is a graph summarizing the results of experiments which show the criticality of the iron concentration in my invention.

The nickel-based composition of my invention contains a dispersed phase of phases of intermetallic compounds comprised of the niobides of nickel, tungsten, and/or molybdenum. The effect of the dispersed phase is to strengthen the alloy particularly at elevated temperatures making it suitable in this respect for exhaust valves. However, while the presence of small amounts of tungsten and molybdenum advantageously form intermetallic compounds with niobium, excessive quantities of these elements lead to rapid corrosion of the alloy in the presence of molten lead oxide or the combustion products of a leaded fuel. For purposes of calculation in the preparation of my alloy it may be said, in general, that tungsten may suitably be incorporated in amounts up to about 5% by weight and molybdenum may be incorporated in amounts up to about 2.5% by weight. However, the quantity of these elements in the final alloy must be controlled such that the value of the atomic percentage of tungsten in the alloy plus the value of the atomic percentage of molybdenum necessarily lies in the range of 0.3 to 1.7%. The rate of corrosion of the nickel-based alloy in the presence of molten lead oxide or lead containing combustion products appears to be a function of the relative number of atoms of tungsten and/or molybdenum present. Because there is a disparity in the atomic weights of the elements incorporated in my alloy, the relative number of tungsten and/or molybdenum atoms may vary substantially even within a rather nar-

row specification for the combined weight percent of tungsten plus molybdenum. Therefore, it is necessary to more specifically define a suitable alloy composition in terms of atomic percentage.

The criticality of the tungsten and molybdenum concentrations in the subject air castable nickel-based alloy was clearly illustrated by a series of experiments, the results of which are summarized in FIGURE 2. These experiments made use of the best known laboratory method

$$0.3 \leq \frac{\frac{\text{Weight Percent Tungsten}}{\text{Atomic Weight Tungsten}} + \frac{\text{Weight Percent Molybdenum}}{\text{Atomic Weight Molybdenum}}}{\frac{\text{Wt. Percent C}}{\text{At. Wt. C}} + \frac{\text{Wt. Percent Si}}{\text{At. Wt. Si}} + \frac{\text{Wt. Percent Mn}}{\text{At. Wt. Mn}} + \frac{\text{Wt. Percent B}}{\text{At. Wt. B}} + \frac{\text{Wt. Percent Cr}}{\text{At. Wt. Cr}} + \frac{\text{Wt. Percent Fe}}{\text{At. Wt. Fe}} + \frac{\text{Wt. Percent Nb}}{\text{At. Wt. Nb}} + \frac{\text{Wt. Percent Ni}}{\text{At. Wt. Ni}} + \frac{\text{Wt. Percent W}}{\text{At. Wt. W}} + \frac{\text{Wt. Percent Mo}}{\text{At. Wt. Mo}}} \times 100 \leq 1.7$$

of evaluating the corrosion resistance of exhaust valve alloys—the lead oxide crucible test. In this test cylindrical specimens 0.444" in diameter by 0.444" long are weighed, placed in a magnesia crucible with 40 grams of lead oxide and heated to 1675° F. for 1 hour. The specimens are then cooled to room temperature, cleaned and reweighed. The loss in weight reflects the relative corrosion resistance of the alloy. While the test involves lead oxide only, experience has shown that favorable results in this test warrant a further study of an alloy in internal combustion engines.

A standard base composition was prepared containing by weight: 0.03% carbon, 0.3% silicon, 0.3% manganese, 6.5% niobium, 20% chromium, 5% iron, the balance substantially all nickel. To this base composition was added various amounts of tungsten and/or molybdenum and specimens subsequently were prepared for use in the above-described lead oxide crucible test. The concentration of molybdenum plus tungsten was expressed in terms of an atomic percent and the weight loss of the specimens was calculated in terms of grams per square decimeter per hour. The results plotted in FIGURE 2 clearly show that concentrations of tungsten plus molybdenum exceeding 1.7% atomic percent result in an order of magnitude increase in the corrosion rate of the alloy. Concentrations of these two elements below about .3% of the atomic percent result in an alloy having unsuitable hot strength for use in exhaust valve alloys.

I have also found that the concentration of iron reaches a critical upper limit from the standpoint of attack by molten lead oxide. A series of experiments similar to those described above were performed using a base composition in which the weight percentage of iron was varied. The base composition consisted by weight of: 0.03% carbon, 0.3% silicon, 0.3% manganese, 3% tungsten, 6.5% niobium, 20% chromium, and the balance nickel. As seen in FIGURE 3, when the iron concentration was increased beyond approximately 10%, the corrosion rate of molten lead oxide as measured by weight loss in grams per square decimeter per hour increased substantially.

Therefore, my air-castable high hot strength lead corrosion resistant alloy may be defined as comprised essentially by weight of: 0 to 0.1% carbon, 0 to 10% iron, 15 to 30% chromium, 4 to 8.5% niobium, 0 to about 5% tungsten, 0 to about 2.5% molybdenum, and the balance substantially all nickel. Small amounts of silicon and/or manganese may be present in the alloy, usually as a consequence of the refining of the iron or other components. Up to 0.7% by weight of each of these noncritical elements may be readily tolerated in the alloy and even 1.0% or 1.5% by weight can be included without adverse effect on the properties of the alloy. It is also known that minute quantities of boron, up to 0.1% by weight, may advantageously be added to high temperature alloys. A further requirement is that the value of the atomic percentage of

tungsten plus the atomic percentage of molybdenum necessarily lies in a range of 0.3% to 1.7%. The weight percentage of tungsten and molybdenum can never be zero at the same time. One may readily determine whether the concentrations of tungsten and/or molybdenum in a given nickel-based alloy are in accordance with my invention by the following simple calculation, knowing the chemical composition of the alloy and the atomic weight of the constituent elements.

Alloys of my invention may be prepared by known techniques. Preferably one would start with a suitable amount of pure molten nickel. To the molten nickel suitable quantities of the other alloying elements may be added to form the final composition. Chromium may be added as pure electrolytic chromium or as the much less expensive ferrochromium. Tungsten may be added as ferrotungsten. Molybdenum may be added either pure or as ferromolybdenum. I have found it advantageous to add niobium as a nickel-niobium alloy comprised of about 55% niobium. Once a complete melt is prepared it may be cast into a useful article such as an exhaust valve at a temperature of about 2950° F. The casting may then advantageously be age hardened at a temperature in the range of 1300–1550° F. for about eight to sixteen hours.

A melt consisting of 0.04% carbon, 0.3% silicon, 0.3% manganese, 8.5% iron, 20% chromium, 6.7% niobium, 3% tungsten and the balance nickel, was formed by the abovedescribed technique. It was subsequently cast into a number of exhaust valves suitable for use in a diesel engine. FIGURE 1 illustrates a typical valve in accordance with my invention. The age hardened and finished valves were placed in a diesel engine, tested, and found to have sufficient hot strength and excellent resistance to attack by the combustion products.

While my invention has been described in certain specific embodiments thereof, it is appreciated that other forms might readily be adapted by one skilled in the art and, therefore, the invention is not to be considered limited only to those embodiments specifically disclosed.

I claim:

1. An air castable nickel base alloy resistant to chemical attack by molten lead oxide consisting essentially by weight of up to 0.1% carbon, a small amount up to 10% iron, 15–30% chromium, 40–8.5% niobium, at least one element selected from the group consisting of tungsten and molybdenum, and the balance nickel, the sum of the atomic percentage of tungsten plus the atomic percentage of molybdenum in the alloy being in the range of 0.3%–1.7%, the amount of tungsten when included in said alloy making up no more than about 5% by weight of said alloy and the amount of molybdenum when included in said alloy making up no more than about 2% by weight of said alloy.

2. An alloy as in claim 1 containing up to about 1% by weight silicon, up to about 1% by weight manganese and up to 0.1% by weight boron.

3. A poppet valve for an internal combustion engine, said valve being formed of an air castable nickel base alloy resistant to chemical attack by the combustion products of leaded internal combustion engine fuels consisting essentially by weight of up to 0.1% carbon, a small amount up to 10% iron, 15–30% chromium, 4.0–8.5% niobium, at least one element selected from the group consisting of tungsten and molybdenum, and the balance

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nickel, the sum of the atomic percentage of tungsten plus the atomic percentage of molybdenum in the alloy being in the range of 0.3%–1.7%, the amount of tungsten when included in said alloy making up no more than about 5% by weight of said alloy and the amount of molybdenum when included in said alloy making up no more than about 2% by weight of said alloy.

4. A poppet valve as in claim 3 containing up to about 1% by weight silicon, up to about 1% by weight manganese and up to 0.1% boron.

5. A poppet valve as in claim 3 wherein the iron content is 2 to 10% by weight and the tungsten content is about 2 to 4% by weight.

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RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

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