[72] [21]	Inventors  Appl. No.	Delmar O. Stanley; John F. Kocis, both of Mentor, Ohio 691,187	[56]	UNIT	References Cited ED STATES PATENTS	
[22] [45] [73]	Filed Patented Assignee	Dec. 18, 1967 Sept. 21, 1971 TRW Inc. Cleveland, Ohio	3,385,739 1,251,341 2,197,955 2,380,821 2,738,267 2,806,782	5/1968 12/1917 4/1940 7/1945 3/1956 9/1957	Danis	148/12.1 75/130.5 X 75/126 148/135 X 148/135 X 75/58 X
[54]	HOT WORKABILITY OF AUSTENITIC STAINLESS STEEL ALLOYS 2 Claims, No Drawings		Primary Examiner—L. Dewayne Rutledge Assistant Examiner—Joseph E. Legru Attorney—Hill, Sherman, Meroni, Gross and Simpson			
[52]	U.S. Cl		ABSTRACT	T: Improv	ring the hot workability by first providing a cast slu	of austenitic
[51]	Int. Cl		trolled mic	rostructure	e, usually by inoculation of	f the molten
[50]						

## HOT WORKABILITY OF AUSTENITIC STAINLESS STEEL ALLOYS

## **BACKGROUND OF THE INVENTION**

#### 1. Field of the Invention

This invention deals with the art of improving the ductility of austenitic stainless steel alloys by controlling the grain size and the secondary dendrite arm spacing in a cast slug which is to be forged, specifically by adding small, controlled amounts of titanium which serve to provide titanium carbonitride compounds in the casting and thereby provide sites for the crystallization of equiaxed grains.

## 2. Description of the Prior Art

The fabrication of exhaust valves for internal combustion engines usually involves one of two methods. The first is that of extruding and coining the valve from a mill wrought valve steel. The second involves casting the valve directly. The advantage of the wrought mill steel for forging processes is that the alloy exhibits good forgeability as a result of the wrought slug ductility. The ductility of the alloy is partially attributed to the breaking down of the cast structure from the ingot stage of mill processing. The disadvantage of this material is the added cost necessary to convert from the ingot stage to bar stock. The cast-type material, on the other hand, can be poured directly into an exhaust valve form and eliminates the cost of working the alloy to bar stock. However, the cast material is more susceptible to defects from casting and is generally much lower in tensile ductility. The material does, however, exhibit good high temperature properties because of 30 its cast structure. This property is desirable in an exhaust valve that is operating at elevated temperatures.

More recently, the desirable properties of the cast and wrought structures have been combined through a process which involves casting the slug from which the forging is to be 35 made, so that some of the cast structure is still retained, particularly in the head portion of the finished valve. This type of technique, however, has been found to present the difficulty of hot tearing, particularly in the region of the outer diameter of the head. The present invention substantially reduces this 40 grains. tendency and provides the advantages of a partially cast, partially wrought structure by providing a slug which has improved forging properties, particularly improved ductility at forging temperatures.

# SUMMARY OF THE INVENTION

The present invention relates to improved forged articles and the method of making the same wherein during the casting of the slug which is to be forged, the microstructure of the austenitic stainless steel alloy is refined to provide a casting having a grain size of from 50 to 400 grains per square inch and a secondary dendrite arm spacing of from 0.02 to 0.06 mm. Experiments have shown that this type of microstructure lends itself particularly well to forging, and substantially reduces the tendency of the forged article to exhibit hot tear-

Although other methods of grain refinement can be used to achieve the purpose of the present invention, we particularly prefer to inoculate the melt with titanium metal, in amounts of from 0.05 to 0.25 percent by weight. Such inoculation results in the distribution of titanium carbonitride compounds throughout the solidified mass, these compounds serving as sites for initiating crystallization of equiaxed grains of the

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

To start with, we should mention that the present invention is applicable to any austenitic stainless steel which is otherwise suitable for use in exhaust valves for internal combustion en- 70 gines. The improved results of the invention, however, are most noticeable when the carbon content is not in excess of about 0.90 percent but is greater than about 0.40 percent, i.e., with medium carbon stainless steel. The grain refinement takes place equally well with higher carbon steels (or more 75 to be necessary for the production of equiaxed grains.

than 0.90 percent carbon) but the improvement in ductility is not as pronounced as it is in the case of the medium carbon

The following analyses set forth typical valve steels which can be benefited by the procedures of the present invention:

TABLE I

Ailloy A	Alloy B	Alloy C
2		
0.475-0.575	0.85-1.05	0.50-0.80
Or ·		
20.00-22.00	20.00-22.00	20.00-22.00
Mn .		
00.01-00.8	4.00-6.00	5.00-7.00
Ni		
3.25-4.50	3.00-3.50	2.00-3.00
Si		
0.25 max.	0.50-0.75	0.50-0.75
3		
0.04-0.09	0.05 max.	0.030 max.
N 0.38-0.50	0.18-0.28	0.20-0.50
Mo ·	1.80-2.20	
3	0.015-0.020	
<i>N</i>	1.0	
<b>V</b>	0.30	
e Pal	D-1	D-1
Bal.	Bal.	Bal.

Once the melt is prepared, the next step consists in refining the grain size of the casting. This can be accomplished by rapid solidification, vibration, by the use of electromagnetic fields, or by the addition of small quantities of selected alloying elements. The latter procedure is the most feasible commercially because of its simplicity. The addition of inoculants to the molten metal can produce grain refinements by restricting grain growth through constitutional supercooling and/or providing foreign nuclei for solidification of fine equiaxed

To be effective, the inoculant should have the following properties:

- 1. stability in solid form in the molten matrix,
- 2. coherency with the matrix, i.e., crystallographic matching for wetting purposes,
- 3. similar density for dispersion, and
- 4. being sufficiently finely divided particles for distribution.

The addition of metals such as titanium, zirconium, vanadium, boron and mischmetal (a mixture of rare earth elements 50 having atomic numbers of 57 through 71 in metallic form, and containing about 50 percent cerium, the remainder being principally lanthanum and neodymium) have been found to provide nuclei formers in the melt with varying degrees of success. By far the most useful metal for this purpose is titanium and the subsequent description of the preferred embodiments will be made in conjunction with that type of inoculant.

In accordance with the present invention, there is provided a cast slug of an austenitic stainless steel alloy inoculated with sufficient amounts of the grain refining additive to refine the grain size to a value of 50 to 400 grains per square inch and a secondary dendrite arm spacing of 0.02 mm. to 0.06 mm. to provide a slug having improved hot forging properties. The preferred grain size is in the range from 200 to 350 grains per 65 square inch. The measurement of the secondary dendrite arm spacing is a measure of segregation and can be carried out on the slug castings according to the technique described by Wallace et al. in "Control of Cast Grain Size," published by the U.S. Army Materials Agency, Watertown, Mass., as technical reference No. AMRA-CR 64-04/1964.

It appears that both constitutional supercooling and independent nucleation are responsible for the grain refinement which occurs. Constitutional supercooling itself reduces the secondary arm spacing, but independent nucleation appears The amount of inoculant can be varied, depending upon the pouring temperature. An amount as small as 0.1 percent by weight is enough to convert a columnar structure to an entirely equiaxed structure at a pouring temperature of 3,000° F. At lower pouring temperatures, even smaller amounts can be 5 used.

A forged valve produced according to the present invention evidences a grain size of from 3 to 6 on the ASTM scale in the most heavily wrought portions thereof, i.e., in the stem, and a coarser grain size of 50 to 400 grains per square inch, and preferably from 200 to 350 grains per square inch in the head portion thereof.

The following specific example illustrates the improvements in the results obtained with the procedure of the present invention.

## **EXAMPLE**

Two identical alloy compositions were made up with a chemistry as set forth in "Alloy C" given above. One was solidified into a columnar structure, and the other was treated with 0.13 percent titanium as an inoculant. The latter was produced in the following manner. The charge was melted and brought to the pouring temperature of 3,040° F. The melt was then deoxidized in the furnace by the addition of 0.25 percent aluminum. The melt was then slagged, followed by inoculation, stirring and pouring. The nontreated alloy slug was found to contain 75 grains per square inch, while that which had been inoculated contained 340 grains per square inch. Both slugs were tested at a temperature of 1,900° F., with a crosshead speed of 4.25 inches per second. The columnar, nontreated slug evidenced a reduction in area of 48.7 percent while that which had been inoculated with titanium to produce an equiaxed structure evidenced a reduction in area of 54.3 percent. The breaking stress for the unrefined material was 35,400 pounds per square inch, while that for the refined material was 33,400 pounds per square inch. The reduction in breaking stress and increase in reduction in area were indicative of an improvement in workability.

The actual processing of valves from these cast slugs confirmed the improvements which had been achieved in the tensile tests. Exhaust valves were extruded and coined at 2,100° from the two types of slugs. In the case of the unrefined casting, external rupturing was quite severe while in the case of the refined material, the rupturing was markedly reduced.

The improvements in workability were obtained by titanium inoculation of medium carbon steels regardless of whether the casting was made with conventional sand castings or with directionally solidified castings as evident from the following table, all measurements being at 1,900° F. and at a crosshead speed of 4.25 inches per second.

Structure	Breaking Temperature(° F.)	Breaking Stress (p.s.i.×10'3)	RA(%:
Sand Base	1,930	35.5	47.5
Sand Base	1,912	36.7	50.3
Sand Base	1,916	34.1	47.3
Sand Equiaxed	1,930	33.6	56.2
Sand Equiaxed	1,916	33.6	53.7
Sand Equiaxed	1,902	32.9	54.0
Chill Base	1,916	36.5	47.2
Chill Base	1,916	30.6	56.4
Chill Base	. 1,912	33.3	51.8
Chill Equiaxed	1,916	29.4	53.9
Chill Equiaxed	1,916	29.7	57.9
Chill Equiaxed	1,907	30.5	51.5

We claim as our invention:

1. An exhaust valve for an internal combustion engine composed of a wrought austenitic stainless steel alloy having a grain size of from 3 to 6 on the ASTM scale in the stem portion and a coarser grain size of 50 to 400 grains per square inch in the head portion thereof, said valve having titanium carbonitride compounds distributed therethrough.

2. The valve of claim 1 in which said coarser grain size is in the range from 200 to 350 grains per square inch.

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