3,698,942 Patented Oct. 17, 1972

1

3,698,942
NOZZLES FOR CONTINUOUS CASTING
David J. Nell, West Mifflin, and Thomas W. Lewis II,
Bethel Park, Pa., assignors to Dresser Industries, Inc.,

Dallas, Tex. No Drawing. Filed Oct. 30, 1967, Ser. No. 679,222 Int. Cl. C04b 41/24

U.S. Cl. 117—123 A

3 Claims

## ABSTRACT OF THE DISCLOSURE

As nozzles for continuous casting, ceramically bonded zircon or zirconia partially impregnated with noncolloidal chromic oxide, zircon, or zirconia particles.

## BACKGROUND

The commercial use of processes for the continuous casting of steel seems destined to make an increasingly important position in contemporary steelmaking. Its many advantages in terms of costs, labor, and simplicity of practice make it very attractive to a highly automated industry.

One of the most important and critical parts or steps in contemporary processes for the continuous casting of steel 25 is considered to be the actual pouring or directing of a carefully regulated stream of molten metal into an initial cooling or "freezing" stage.

Generally, the molten metal is fed from a ladle to what is called a tundish ladle. The purpose of the tundish ladle 30 is to maintain a uniform ferrostatic head. The nozzle opens from a lower portion of the tundish. It is this nozzle which is so critical and important to controlling flow rate and stream cross-section to the cooling stage mold. It must be characterized by resistance to skulling. "Skulling" can 35 be defined as localized build-up of solidified metal and slag on interior surfaces of the nozzle and about its exit orifice.

The nozzle must be substantially inert to the molten metal and slag passing through it. If it is not inert, there will be erosion or corrosion of interior nozzle walls and a 40 change in the characteristics of the nozzle orifice, thereby also disadvantageously modifying and changing evolving stream configuration and volume.

The nozzle must have good thermal shock resistance. It is not practical to heat the nozzle to the temperature of 45 molten steel prior to contacting the nozzle with molten steel. There is usually a substantially difference in temperatures when the molten steel first touches the nozzle, for example, 800 to 1200° F.

It has been found that denser nozzles are more prone to thermal shock because they have a less yielding microstructure. Also, they are more prone to skulling as they have higher thermal conductivity. On the other hand, denser refractories have better resistance to slag and metal attack or erosion.

It is an object of this invention to provide a nozzle for continuous casting of steel which has improved thermal shock resistance, resistance to skulling, and improved resistance to slag and metal erosion.

# BRIEF DESCRIPTION

A nozzle for use in continuous casting of steel consists essentially of a tubular shape usually having a relatively large top opening converging to an exit orifice at its bottom. According to this invention, nozzles are porous 65 ceramically bonded zircon or zirconia compositions which are partially impregnated with noncolloidal chromic oxide, zirconia, or zircon particles. By porous is meant 10 to 30% porosity.

The zirconia refractory suitable for use according to this 70 invention is what is known as partially stabilized. By partially stabilized, we mean normally at least about 70%

2

stabilized. In any event, one skilled in the art understands the degree of stabilization necessary to overcome the problems of changes in crystallinity. Stabilized zirconia is zirconia substantially entirely exhibiting a cubic crystallized structure, the individual crystals of which are "propped," to prevent their disintegration at lower temperatures. For example, calcium oxide is conventionally used to produce a stabilized zirconia refractory material. In practice, stabilization is brought about in one method by mixing from 3 to 6%, by weight, of 99% pure calcium oxide with 97 to 94% zirconia. Other materials such as magnesia and yttria have been used to stabilize zirconia.

Zircon refractories are refractories made substantially entirely from zircon or zirconium metasilicate. The properties of zircon refractories can be altered somewhat by making various additions such as silica, mullite, chromic oxide and so on.

The particular refractory oxides used for impregnation, according to this invention, range in size from about 0.1 micron to about 5 microns. Preferably, the particles range in size from 0.5 to about 5 microns.

#### DETAILED DESCRIPTION

Further features and other objects and advantages of this invention will become clear to those skilled in the art by a careful study of the following detailed description. In the following description and in the claims, all percentages, ratios, and parts are by weight.

Nozzles according to the teaching of this invention are manufactured by first manufacturing a ceramically bonded zircon or zirconia nozzle shape by conventional techniques. That is, they are prepared from a size-graded refractory batch formed into shapes, for example, by pressing with the aid of a temporary binder, and burned at temperatures sufficient to provide a ceramic bond. Zirconia refractories typically have a major portion of their open and connected pores with a minimum size that ranges from 9 to 45 microns. The pores of zircon refractories are noticeably smaller and range from a minimum of about 4 to 15 mircons. This is because zircon brick are generally prepared from batches having a finer particles size distribution.

The nozzles are then impregnated by immersing them in a suspension of noncolloidal ceramic particles, agitating or vibrating the suspension for a period sufficient to impregnate at least the surface of the nozzles. The suspension, for example, is prepared by mixing the noncolloidal particles with from about 50 to 90% of a suitable carrier fluid. A readily available carrier fluid is water. It has been found desirable to prepare the slurry using a dispersing agent appropriate to both the noncolloidal particles and the carrier fluid. The agitation or vibration can be applied in a number of ways, for example, mechanically. Frequency of vibration can range from about 20 cycles/ sec. to ultrasonic vibrations in the range of 40 kcs./sec. The amplitude of vibration is usually limited by the equipment. However, it has been found for a given frequency the largest possible amplitude is desirable.

According to the preferred embodiment of this invention, a zircon refractory is prepared from a size-graded batch consisting essentially of 95% zircon and 5% ball clay. The batch is tempered with a temporary binder and pressed into nozzle shapes. They burn at approximately 2700° F. to a density of about 225 lbs./cu./ft. and have an apparent porosity of approximately 20%.

The preferred nozzles were placed on the 20% aqueous suspension of pigment grade chromic oxide which was prepared by blending the chromic oxide into water with the aid of a sodium phosphate dispersent. The zircon nozzles was immersed in the supension and the suspension was vibrated at 60 cycles/sec. for about 30 minutes. The zircon nozzle was penetrated to a depth of about \(^{1}\)/6 to

3

1/8 inch with the chromic oxide. Through some phenomenon not entirely understood, the bore of the nozzle was better impregnated than the outer surfaces which is, of course, fortunate.

Nozzles made according to the teachings of this invention have decreased surface porosity and, therefore, are more resistant to erosion and corrosion by slags. However, their overall density is not substantially increased and, therefore, their thermal conductivity remains about the same. Therefore, their resistance to skulling is not decreased. Furthermore, since the overall density of the nozzles is not increased, their tendency towards thermal spalling is not increased.

Having thus described the invention in detail and with sufficient particularity as to enable those skilled in the 15 art to practice it, what is desired to have protected by Letters Patent is set forth in the following claims.

We claim:

1. Nozzles for use in continuous casting of steel, said nozzle being porous and consisting essentially of ceramically bonded refractory oxides selected from the group

4

consisting of zirconia and zircon, said nozzle impregnated to a depth of at least about  $\frac{1}{16}$ " from the surface with noncolloidal refractory particles selected from the group consisting of chromic oxide, zirconia, and zircon.

- 2. Nozzle according to claim 1 in which the nozzle has a pore diameter predominantly between 5 and 100 microns.
- 3. The nozzle according to claim 1 in which the noncolloidal particles range in size between about .1 and 5 microns

#### References Cited

### **UNITED STATES PATENTS**

2,809,126 10/1957 Murphy et al. \_\_\_\_ 117—125 X 2,874,071 2/1959 Kadisch et al. \_\_\_\_ 117—123 A

ALFRED L. LEAVITT, Primary Examiner J. R. BATTEN, Jr., Assistant Examiner

U.S. Cl. X.R.

117-125, 169 R