Efficacy of Gas Purging for Titanium Casting

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Oxygen density in the melting atmosphere, oxygen uptake, hardness and castability of pure titanium castings were examined to evaluate the efficacy of gas purging in reducing contamination from the melting atmosphere and mold, using a newly developed titanium casting machine in which the double purging process is systematized. The adoption of a double purging operation resulted in an extremely low oxygen density in the melting atmosphere, followed by extremely low oxygen uptake in the casting when compared with the conventional titanium casting machine. When the purging operation was used, the surface hardness was markedly reduced, although there was no difference in castability. From these results, it was suggested that the newly developed titanium casting machine with the double purging operation could produce better titanium castings with less contamination due to the mold and gas impurities in melting atmosphere.

Key words : Dental casting, Titanium, Casting machine

INTRODUCTION

Over the past decade, significant developments have been made in the dental casting of titanium and its alloys, and several casting systems are now available commercially¹⁻³⁾. Although an inert atmosphere is commonly used in those systems¹⁾, titanium and its alloys are often susceptible to contamination with atmospheric gas and mold components during melting and casting. As titanium is highly reactive at high temperatures, it can easily be oxidized and dissolve such elements as oxygen, nitrogen and hydrogen.

Several investigators⁴⁻⁷⁾ have demonstrated that such potential contamination from the melting atmosphere might easily cause the deterioration of mechanical properties in titanium castings. Yoneyama *et al.*⁴⁾ reported the effect of the vacuum degree in the melting chamber on the mechanical properties of pure titanium castings, and Hamanaka¹⁾ described that the most efficient method for replacing the air in the chambers with an inert gas is repeating the evacuation-a gas flooding process. Tamaki *et al.*⁵⁾ also showed that increasing the number of repetitions of an exhaust and argon gas inflow process is more effective in producing titanium castings with less contamination.

A new titanium casting machine was developed, which has two significant characteristics of a double gas purging operation and a highly differential gas pressure for casting. In this study, the efficacy of purging was examined in terms of oxygen density in the melting atmosphere, oxygen uptake and hardness of pure titanium castings, and castability of titanium.

MATERIALS AND METHODS

Fig. 1 shows the external view of the newly developed casting machine* for titanium and its alloys (Code : MC). It has a two-chamber structure, consisting of an upper melting chamber and a lower casting chamber, and is principally a type of argon-arc melting and suction-argon gas pressure casting with a low temperature mold. The schematic operation diagram is shown in Fig. 2. The main features of the machine are as follows : (1) the chambers and mold are dried and purged of air and gas impurities by the double purging process consisting of evacuation of the chambers through the mold and subsequent argon gas inflow twice, and (2) a highly differential casting pressure (7kgf/cm² at maximum).

Oxygen density in the melting atmosphere was measured through each step of the

Fig. 1 External view of the newly developed casting machine.

Fig. 2 Schematic diagram of pressurizing operation for the melting chamber of the machine.

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Fig. 3 Wax pattern for castability test.

purging operation using an oxygen analyzer**, which was set in the melting chamber of a prototype of the casting machine MC. Oxygen content in titanium castings ($3^{\circ} \times 20$ mm), the surface of which was slightly sandblasted with $50 \mu\text{m Al}_2\text{O}_3$, was determined with a nitrogen/oxygen determinator#. For comparison, another arc-melting and suction-pressure casting machine## (Code: CA) which uses a process of evacuation and subsequent argon gas inflow for once, was used.

Hardness measurements were made at several points from the surface to the interior on the cross-section of titanium castings ($10 \times 10 \times 6$ mm), using a Vickers microhardness tester@ with a load of 500 g and a loading time of 15s.

For the castability test, wax mesh patterns@@ (26×35 mm) with 119 segments were prepared with or without air vents, as shown in Fig. 3. The castability was evaluated with the ratio of cast titanium segments to the total number of segments in the wax pattern.

Pure titanium ingots\$, JIS grade 2 (oxygen content; 1150 ppm from the inspection certificate of the manufacturer) and a phosphate-bonded investment material\$\$ specified for the casting machine MC were used for casting. The investment material was mixed, heated according to the manufacturer's instructions, and then cooled to room temperature before casting. In casting with CA for comparison of the oxygen uptake in the casting, an investment specified for CA was used and the preparation of the mold followed the manufacturer's instructions. Three specimens were prepared for each of the oxygen determination, hardness test and castability test.

RESULTS

Oxygen density in the melting chamber of the new casting machine MC was 34 ppm at a minimum during the first gas purging step, and fell down to 7 ppm at the second purging step. Fig. 4 shows the changes in oxygen content in pure titanium casting with the purging

** LC700L, TORAY, Tokyo, Japan

TC-136, LECO Corp, Michigan, U. S. A.

CYCLARC, J. MORITA Co., Kyoto, Japan

@ MVK-D, AKASHI, Tokyo, Japan

@@ Nobil-mesh wax 3001 diamond heavy, Nobilium/American Gold, New York, U. S. A.

\$ TB35H, Nippon Stainless Steel Co., Tokyo, Japan

\$\$ Super Vest-D, Okazaki Minerals and Refining Co., Osaka, Japan

operation, together with content when the other casting machine CA was used. The oxygen uptake in the casting was more than 120 ppm when the casting was made without purging. This was significantly decreased by the purging operation, being about 30 ppm after the single purging and 6 ppm after the double purging on average. Although there was no significant difference in the oxygen content between the single and double purging operations, the deviation in the content became markedly smaller with the double purging. In the casting machine CA, the oxygen uptake was about 100 ppm.

Fig. 5 shows the microhardness distribution of the castings. The outermost surface was harder than the interior, where hardness reached constant values. Such surface hardening was marked when the non-purging operation was used, while there was little difference between the single and double purging operations.

The castabilities of titanium under the different conditions are shown in Fig. 6. No improvement in castability was observed by repeating the purging operation independently of

Fig. 4 Oxygen content in the castings obtained after purging operation.

Fig. 5 Hardness distribution of the castings obtained after purging operation.

Fig. 6 Castability of titanium.

the addition of air venting.

DISCUSSION

A common method for preventing oxidation or other atmospheric attack in titanium casting is to employ an inert gaseous atmosphere in the melting chamber or in all chambers. Several investigators⁴⁻⁶⁾ have suggested that it would be important to repeat a series of evacuation and argon gas inflow processes as the residual air due to insufficient air exhaust or replacement with argon gas might cause contamination during melting and casting, resulting in the embrittlement of titanium castings. In the newly developed casting machine MC, the double gas purging system is incorporated, in which a cycle of evacuation followed by argon gas inflow is repeated twice. It was found that the oxygen in the melting chamber could be reduced to 34 ppm by the first purging and to as low as 7 ppm by the second purging in this system. As the purging process is performed through the mold in the casting chamber, it may also be effective for purging the air in the mold as well as for drying the mold. Consequently, the oxygen uptake in the resultant titanium casting could be significantly reduced. The oxygen content in the casting was 30 ppm when the single purging operation was applied and only 6 ppm when the double purging operation was applied. The process in the conventional titanium casting machines that the chamber is once evacuated and filled with argon gas prior to melting the ingot may be analogous in principle to the single purging process in MC. However, the oxygen uptake in the casting with one of the conventional casting machine CA was much higher than that obtained after the single purging with MC. It has been reported that the potential contamination of the casting would be affected by the vacuum degree in the melting chamber due to the use of different vacuum pumps⁴⁻⁶⁾ and argon gas flow rate⁷⁾. In addition to such factors, the low mold temperature employed in MC may have favorably restrained the reaction of titanium with oxygen. The double purging operation appeared to be sufficient for minimizing oxygen contamination in the melting and

casting chambers in MC, differing from the results of previous reports using the other casting machines^{4,5}).

Generally, the mechanical properties, of cast titanium are greatly affected by the oxygen content in the casting⁸; the tensile strength increases and elongation decreases with increases in oxygen content. Hamanaka *et al.*⁹ and Yoneyama *et al.*⁴ reported that the tensile strength and elongation of cast titanium varied with use of different casting machines and different vacuum degrees, and that this might be partly attributed to the different residual oxygen contents in the melting atmosphere causing oxidation and oxygen uptake. The existence of a hardened or reacted layer in the surface of titanium castings has also been reported^{8,10-14}). This layer has been found to embrittle the casting because it is hardened by oxygen uptake and may include cracks^{10,11}), and it is considered to be materially undesirable for titanium casting¹⁴). In the present study, surface hardening of the casting was observed from the hardness test, and the surface hardening was marked when no purging operation was applied. A significant decrease in the surface hardness was found in castings obtained after the first purging operation, although no effect of purging appeared on the internal hardness of the casting. The hardness showed no further decrease by the second purging operation. The formation of the reacted layer of the casting in the mold is attributed to the contact with the investment, and can be diminished by lowering the mold temperature or selecting the investment composition^{5,10-13}). Oxygen may also contribute to the formation of the reacted layer¹¹). As the low temperature mold is employed in the casting system of MC, it is considered that the reaction of the molten titanium with the mold and atmosphere may be inherently restrained to some degree. Moreover, the purging operation could effectively reduce the oxygen density in the melting and casting atmosphere as well as the oxygen uptake in the casting. Although it is not known whether the oxygen in the atmosphere during melting and casting may react with titanium primarily from surface oxidation or solid solution, or may partly control the rate of reaction of molten titanium with the mold, the reduction in oxygen content in turn resulted in a significant decrease in surface hardness. However, the purging operation showed no further decrease in the hardness. This indicates that changes in oxygen content below the level of 30 ppm would have no practical effect on the hardness. On the other hand, the hardened layer was still observed in the surface area even although the oxygen content in the casting was reduced to as low as 6 ppm. The investment material used was of a phosphate-bonded type specified for the casting machine MC, and the hardened layer might have formed by the reaction with silicon¹⁵) or some other components from the investment mold. The purging operation employed in MC was found to be sufficient for minimizing the change in hardness, although some reaction with the mold might be unavoidable as long as the phosphate-bonded investment is used.

The castability of molten titanium has been considered to be affected by contamination due to the mold¹⁶). Tamaki *et al.*¹⁷) and Matsuda *et al.*¹⁸) reported that the newly developed casting machine MC could produce satisfactory titanium castings in appearance with good castability and less external casting defect for simple plate or clinical metal framework for denture base use. In the present study, the effect of the repeated purging operations on castability was examined using mesh patterns. The results showed no clear difference in castability between the single and double purging operations. This is probably because the

casting pressure in MC was large enough to negate the effect of the purging operation if any.

CONCLUSION

Oxygen density in the melting atmosphere, oxygen uptake, hardness and castability of pure titanium castings were examined to evaluate the efficacy of the gas purging operation in minimizing contamination from the melting atmosphere and mold, using a newly developed titanium casting machine with a systematic double purging process. Oxygen density in the melting chamber was 34 ppm during the first purging step, and was reduced to as low as 7 ppm by the second purging operation. The oxygen content in the casting tended to decrease with repetition of the purging operation. The new casting machine significantly reduced the oxygen uptake in the casting by the purging operation when compared with the conventional titanium casting machine. When the purging operation was used, the surface hardness was markedly reduced, although there was no difference in castability. From these results, it was suggested that the newly developed titanium casting machine with the double purging operation could produce better titanium castings with less contamination due to components of the mold and gas impurities from the melting atmosphere.

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HEMA プライマーへの各種銅塩の添加効果を検討した。ウシ象牙質表面を 10 %リン酸水溶液で処理した後、銅塩を含む 35 % HEMA 水溶液プライマーを塗布し、MMA-TBB レジンでアクリル棒を接着した。銅塩の種類・濃度を変えて接着したところ、プライマー中の銅塩の最適濃度は $0.5\text{--}3.0\mu\text{mol/g}$ であった。検討した 8 種類の銅塩の中で、硫酸、メタクリル酸、メタクリロイルオキシエチルフタル酸、メタクリロイルオキシエチルコハ

ク酸の銅塩が特に有効であり、 $14.2\text{--}16.1\text{MPa}$ の平均接着強さおよび最低の接着強さの平均値として $9.9\text{--}11.7\text{MPa}$ が得られた。これらの接着強さは、市販の 4-META/MMA-TBB レジン接着システムで得られる値よりも大きかった。ある種の銅塩存在下で重合したポリ MMA の分子量が増加したことから、いくつかの銅塩では MMA-TBB レジンに対するその分子量増加効果によって接着強さが向上したことが示唆された。

光重合コンポジットレジンの重合性に及ぼす光強度の影響

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照射距離を変化させて得られた種々の光強度で光重合コンポジットレジンを重合し、硬化深さを初め硬化体内部の反応率、重合率およびペンダント二重結合量の深さ方向に対する分布を測定し、これら重合特性に及ぼす光強度の影響を調べた。照射する照射量（光強度と照射時間の積）を一定にすると光強度、照射時間に関わらず硬

化深さはほぼ一定の値を示し、硬化体内部の反応率、重合率およびペンダント二重結合量の各分布もよく一致した。硬化深さは照射量の対数で表され、この直線回帰式から使用した光照射器に対する材料の吸光係数および材料が硬化するのに必要な照射量（臨界照射量）を求めることができた。

チタン鑄造におけるガスパーズの効果

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溶解雰囲気と鑄型内のガス清浄化を目的としたダブルガスパーズを特徴として開発されたチタン専用鑄造機を用い、ダブルパーズの効果について検討することを目的に、溶解室雰囲気中ならびに純チタン鑄造体中の酸素濃度分析、鑄造体の硬さ試験および鑄造性試験を行った。ダブルパーズを採用することで溶解雰囲気の極低酸素化が可能となり、純チタン鑄造体中の酸素量は他機種に比

べて著しく低くなった。さらにチタン鑄造体表面の硬さもパーズを採用することで減少した。しかし、鑄造性に対しては影響はみられなかった。以上の結果から、ダブルパーズを採用して開発されたチタン鑄造機により酸素の混入を抑えたチタン鑄造体を作製できることが示された。