Technical note

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Possible Segregation Caused by Centrifugal Titanium Casting

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The possibility of the segregation under solidification process using a centrifugal casting machine was investigated using an electron probe microanalyzer with elemental distribution map, line analysis and quantitative analysis. When a very small quantity of platinum was added to local molten titanium during the casting process, macroscopic segregation was observed under conditions of density difference of 0.1g/cm^3 at the most, confirming that the centrifugal force of the casting machine is extremely strong. When a Ti -6Al-4V alloy was cast, however, no macroscopic segregation was observed. The centrifugal force of the casting machine examined in the present study hardly results in the body-force segregation in this titanium alloy.

Key words: Titanium alloy, Centrifugal casting, Segregation

INTRODUCTION

Titanium casting machines for dental purposes have been developed continuously over the last decade[1]. To obtain a complete titanium casting, intense casting force is required because its solidus temperature is very high and, as a result, the molten titanium tends to solidify very quickly during casting. As previously reported[2], the centrifugal machine is presumed to generate extremely strong centrifugal force, probably 100 or 1000 times that of gravity. Therefore, the possibility that such a strong force must yield a macroscopic segregation, or a body-force segregation, in the case of a titanium alloy, for example Ti-6Al -4V has been discussed. Usually, any segregation results in undesirable change in casting character, such as hardness and corrosion, as compared with homogeneous distribution.

As is known, segregation is responsible mainly for the density difference of each portion within liquid or between liquid and solidified particles. Since available ingots of Ti-6Al-4V alloy are practically homogeneous, the dominant reason is presumed to be the latter which takes place during solidification. Even if the density difference is appreciably small, an extremely strong centrifugal force may cause the segregation.

On the other hand, there are some conditions under which the segregation hardly occurs in dental application. One condition originates from the very short solidification time in a mold cavity, as a result of which, the liquid and the solidified particles can coexist only for very short time.

Only experimental findings can claim the settlement because positive and negative conditions exist in regard to segregation in centrifugal casting of titanium. In spite of the

critical importance of casting design, this subject has remained unstudied due to experimental difficulties which involve the estimation of both the true centrifugal force during casting and solidification time.

The present study investigated the possibility of segregation in Ti-6Al-4V alloy under strong centrifugal force. The elemental analyses, involving map, line and point, were conducted using an electron probe microanalyzer (EPMA). For this purpose, the following experiments were carried out. First, the intensity of the centrifugal force was compared with gravity and estimated by means of the tracer element molten method developed by the authors[3,4]. Then, the titanium alloy was cast, and the distributions of aluminum and vanadium were investigated in the vicinity of the inlet part and the front part of the casting.

MATERIALS AND METHODS

As shown in Fig. 1, a rod-like wax pattern, 6mm in diameter and 30mm in length, was prepared and attached to the crucible.

For the casting of pure titanium, a platinum wire of 0.5mm in diameter was inserted into the wax sprue near the crucible. Platinum was selected as a tracer because of its large density, high melting temperature and because it is free from oxidation at high temperatures. When the molten titanium contacts the platinum wire, it is melted and the Pt atoms are carried away by the titanium flow and are scattered in the casting. The Pt distribution visualizes the titanium flow pattern and moreover, indicates the intensity of the body force from the anomalous pattern if segregation occurs.

The prepared patterns were invested with a commercial phosphate-bonded investment*.

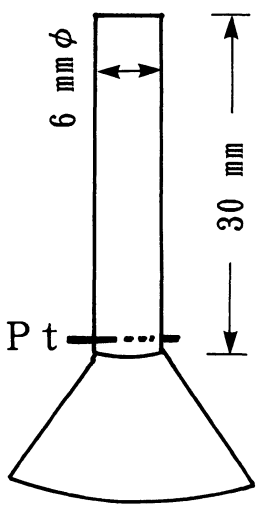

Fig. 1 Prepared wax pattern.

* Titanium Vest II, Ohara Co. Ltd., Osaka, Japan

According to the manufacture's instructions, the molds were heated to 1,150°C and cooled slowly to room temperature in an electric furnace. A commercial pure titanium and Ti-6Al-4V alloy were cast using an argon arc centrifugal casting machine**. The chemical composition of this alloy is 88.10Ti-6.75Al-4.50V-0.20O and others (manufacturer's indication). To compare the centrifugal casting machine, a one-chamber pressure casting machine# was also used according to the manufacturer's recommendation. Three castings of each metal were produced in order to investigate the reproducibility of experimental results.

After sand blasting and short chemical pickling, the castings were cut transversely or longitudinally. These sections were analyzed through an EPMA## equipped with HII mapping system. Elemental mapping analyses were carried out with stage scan mode. Accelerating voltage was 20 kV, specimen current was 0.5μA and measuring interval at each step was 0.03 sec. Line analyses were carried out in an ordinary manner. Quantitative analyses were carried out with the alloy ingot as a reference standard and corrected by the three major matrix effects: atomic number (Z), absorption (A), and fluorescence (F), which are commonly called the ZAF method[5]. Electron beam diameter in this analysis was chosen as 3 micrometers to avoid the variation of the very fine structure arising from the crystal growth.

RESULTS

Fig. 2 shows the typical Pt distribution maps of the longitudinal and the transverse sections of the cylindrical casting made by the pressure casting machine. The number of each transverse section corresponds to that of the longitudinal section. Pt was not detected in about lower half of this casting. This indicates that the initial half influx flowed before the platinum wire was melted. In the transverse sections, a vortex can be observed which is known as the sink vortex. Pt content even at the highest portion was deduced to be about 0.5 mass% from the X-ray count of the mapping analysis. This implies that the density difference between molten titanium with and without Pt, is about 0.1 g/cm^3 at the most. Segregation of Pt caused by this density difference in liquid cannot be observed, because the gravity, one of the body force which is the important factor in segregation, is very small. In this case, the tracer element (Pt) indicates only the trace lines of the filling flow.

Fig. 3 shows the typical Pt distribution maps of the longitudinal and the transverse sections of the cylindrical casting made by the centrifugal machine. The numbers of the transverse sections correspond to those attached to the longitudinal section. As can be seen from the longitudinal section, the surface layer of about 0.5 mm thickness was dark in the lower half, which indicates that no platinum was present in this layer. This is confirmed by the transverse section maps, which indicate Pt-poor outermost rings. The formation of this black shell demonstrates that the initial influx without platinum filled the cavity up to number 4 level in this figure, and instantly solidified only in the outermost layer in contact with the cavity wall. In contrast, in the inner area, the closer a position gets to the front end,

** Titaniumer VF, Ohara Co. Ltd., Osaka, Japan
# Auto Cast HC-III, GC Co. Ltd., Tokyo, Japan
EPMA 8705, Shimazu Co. Ltd., Kyoto, Japan

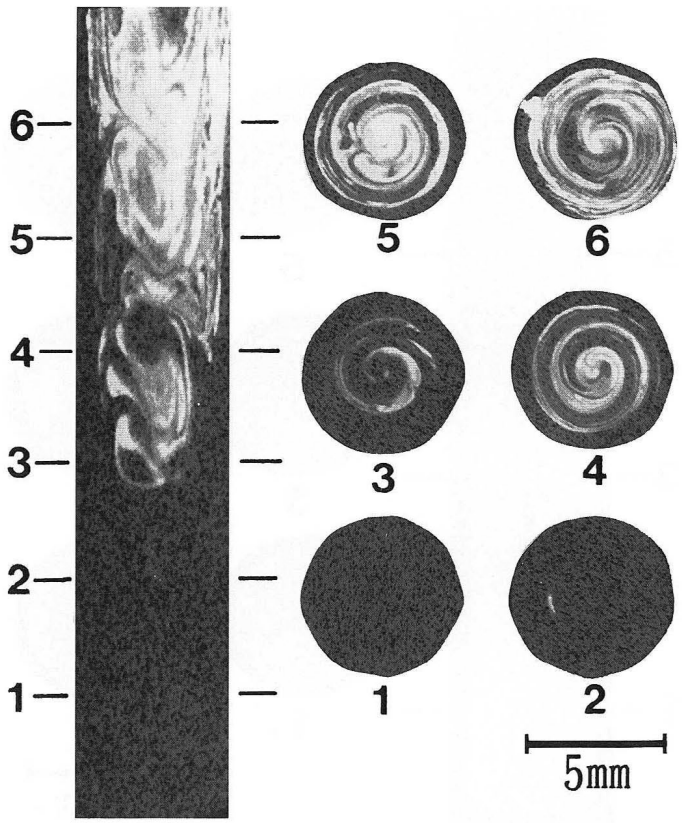

Fig. 2 Pt distribution maps of longitudinal and transverse sections cast by one chamber pressure casting machine. The numbers of the longitudinal map correspond to those of transverse sections. These Pt distributions express the flow pattern produced by the filling process.

the higher the Pt content. This indicates the segregation occurs by the centrifugal force acting downward (arrow); the denser liquid containing a small quantity of platinum was forced to move to the front end by the centrifugal force. The segregation was enhanced by the longer solidification time in the inner area because the heat flux from the molten titanium to the mold was hindered by the solid shell which has low thermal conductivity[6]. Thus, it is confirmed that the centrifugal force is extremely strong compared with gravity and may cause body force segregation even if the density difference in liquid of a titanium alloy is slight.

Fig. 4 shows the typical elemental mappings of the Ti-6Al-4V alloy casting. The upper two maps were obtained from the influx part which corresponds to the number 6 portion in Fig. 3, and the lower maps, the front part which corresponds to the number 1 portion in Fig. 3. All these maps were raw data, which means that any artificial treatment, such as background

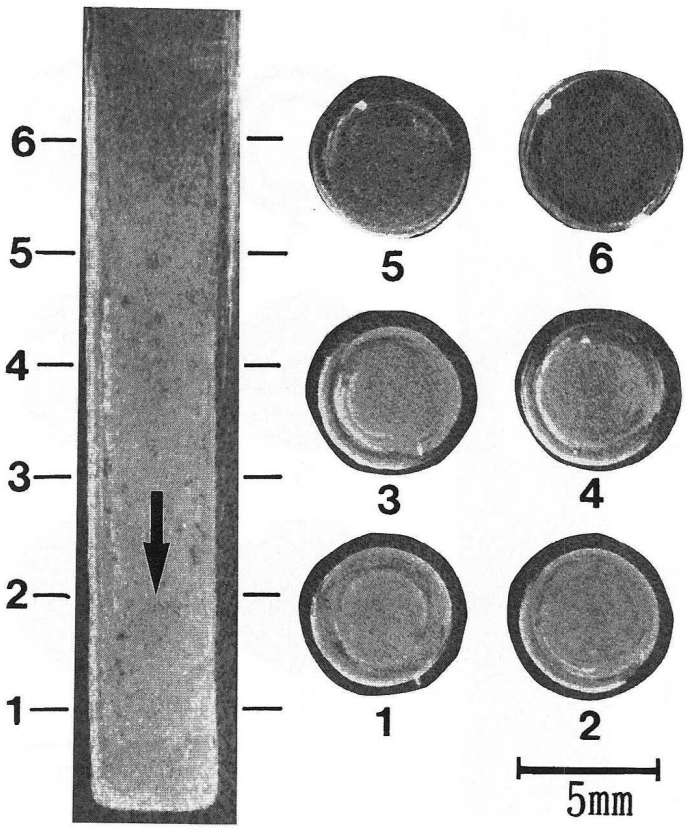

Fig. 3 Pt distribution maps of longitudinal and transverse sections cast by centrifugal casting machine. The numbes of the longitudinal map correspond to those of transverse sections. The arrow in the longitudinal map indicates the direction of the centrifugal force. These Pt distributions express not the flow pattern but the segregation following the filling of the cavity.

reducing, was not carried out. As can be seen, the distribution of the aluminum is homogeneous. The distribution of vanadium is also homogeneous as a whole, while microscopic distribution originating from crystal growth can be detected.

Fig. 5 indicates line analyses along the center line of each photograph shown in Fig. 4. The influx and the front parts are shown on the left and the right sides, respectively. Despite the dendritic segregation pattern of vanadium (Fig. 4), the variation of vanadium content was not so large, being within about 0.1%. Not only the Al but also the V content is macroscopically homogeneous and indicates no difference in the analyzed portion.

Quantitative analyses of the Al and V were carried out at both portions in Fig. 4. X-ray intensities were measured at 5 arbitrary points in each portion and corrected by means of ZAF. This measurement was repeated twice using different rod castings made by centrifu-

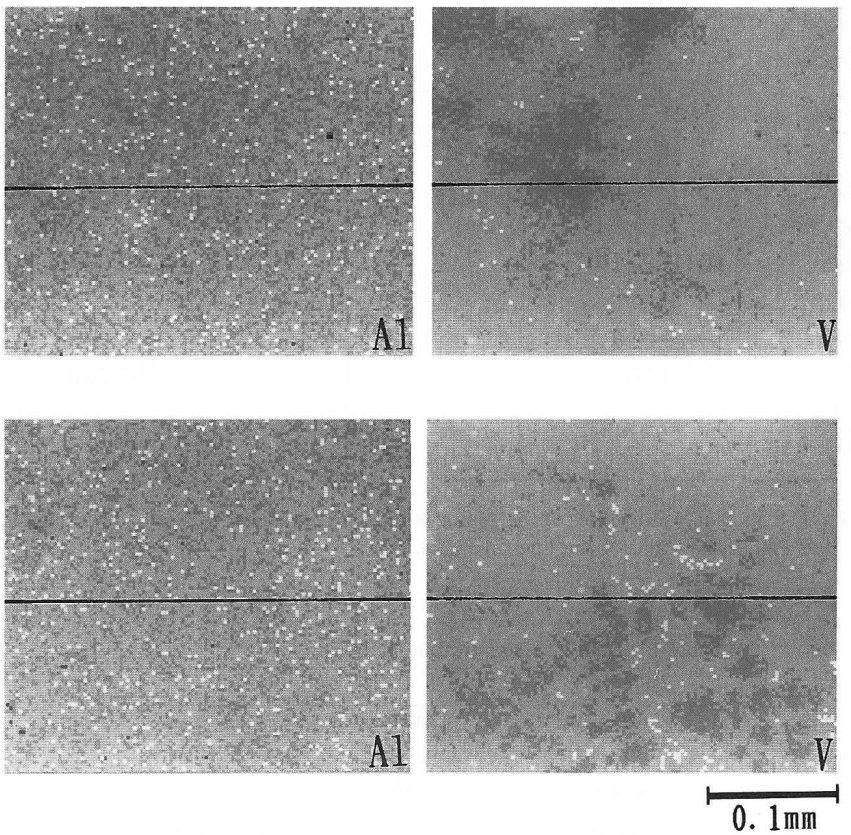

Fig. 4 Al and V distribution maps of the Ti-6Al-4V casting. The upper two were obtained from the influx part and the lower two, from the front part.

gal casting. Obtained data are shown in Table 1. In general, the final precision of EPMA is known up to the order of 0.1%, but this includes both the factor of sample homogeneity and instrument factors, such as drift of electronic components[7]. In this measurement, the desired information was the change in content depending on the position, so the representation up to 0.01 mass% order is permissible via statistics. No significant difference in Al and V contents at the front portion and the influx portion was obtained from the Student t-test. In conclusion, the centrifugal casting did not induce the segregation of the Al and V for Ti -6Al-4V alloy in dental usage.

DISCUSSION

It is known as gravity segregation that if there is density difference in the liquid state, denser portions accumulate to the direction of the force. This phenomenon is observed not only in dispersal of particles in a liquid but also in the aggregation of liquid mixtures. The extent

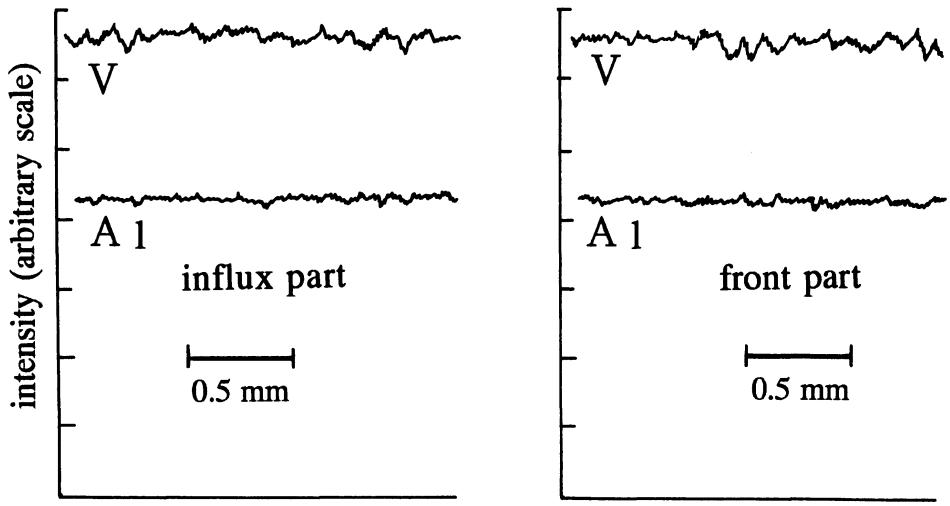

Fig. 5 The line analysis profiles of the Al and V along the lines in Fig. 4. The detecting distance is longer than that of the lines in Fig. 4.

Table 1 Result of quantitative analysis

Sample 1	Al	V
influx part	6.53±0.03	4.65±0.08
front part	6.51±0.02	4.70±0.07
Sample 2	Al	V
influx part	6.55±0.01	4.70±0.08
front part	6.54±0.02	4.80±0.07

(mass% Mean±S.D., n=5)

of segregation depends on several factors including the degree of density difference, the magnitude of body force, such as gravity and centrifugal force, and the working interval of the liquid state.

In industrial fields, segregation has often been observed when alloys solidify under gravity or centrifugal force. By application of this phenomenon, functionally gradient composite Al-Cr alloys were fabricated[8]. In most cases, however, solidification time is in some tens of seconds.

In the dental titanium casting, however, solidification time is presumed to be of the order of 0.1 sec, therefore; true conditions governing the segregation cannot be expected but can be determined only by the experiment devised by the authors. The first experiment was carried out in order to obtain the standard distribution (titanium flow pattern) of the tracer by means of the pressure casting. In this condition, even if there is appreciable density difference in the liquid, segregation hardly occurs (Fig. 2) because gravity is comparatively low. The second experiment was carried out in order to estimate the true cooperative

condition influencing the macroscopic segregation in this centrifugal casting machine. In this case, clear segregation was observed in the inner part of rod casting (Fig. 3).

Regarding Ti-6Al-4V alloy, segregation was not observed in the rod castings made by the centrifugal machine. The rod cavity was chosen for two reasons; one is that the direction of the centrifugal force can coincide with the long axis of the rod and the other is that the rod, having a 6mm diameter, causes a longer solidification interval. As mentioned above, segregation could not be found in the titanium alloy under such extreme conditions. In conclusion, the degree of segregation in this titanium alloy was negligible under the conditions of dental applications.

CONCLUSION

Titanium castings subjected to a large centrifugal force during solidification were compared with those obtained by a pressure casting machine, and were discussed regarding their segregation. When a very small density difference of molten titanium was induced by platinum wire, migration of higher density parts was observed due to centrifugal force. However, even this strong centrifugal force did not cause macroscopic segregation of Ti-6Al-4V alloy in dental casting.

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た，各測定時の象牙質窩洞辺縁部の間隙とテフロン製窩洞辺縁部の間隙の差は，水中浸漬期間が増加するに伴い減少し，せん断接着強さが向上した結果から，経時的経過に伴う硬化反応の進行による接着強さの向上も適合性改善に影響していると考えられた．

種々の表面あらさを有するコンポジットレジンへの口腔レンサ球菌の付着性

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コンポジットレジンに口腔細菌が付着することによって2次カリエスが生じる．本検索は上顎第1大臼歯に装置したコンポジットレジン片から優位に分離されたS. oralisの種々の表面あらさを有するコンポジットレジンへの付着性を検討した．供試コンポジットレジンは市販のものを使用し，スクロール非存在下で細菌付着性試験を行った．また供試コンポジットレジンの表面あらさ値は0.2 μm～3μmであった．その結果，S. oralisはフィラーに付着していたことから，表面あらさと細菌付着性との間に相関性は認められなかった．

牛歯象牙質の引張強さに及ぼす冷凍保管と煮沸の影響

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歯科材料の実験に人歯の代替材料として牛歯が多く使用されているが，大量の牛歯を一度に処理するのは困難であるため，試験に供せられる前に何らかの形で保管されているのが現状と考えられる．そこで，本研究では，冷凍保管した牛歯と比較のために沸騰水で煮沸した牛歯の引張強さを検討した．

抜歯直後と冷凍庫内にて1週間，4週間，1年間の保管，もしくは沸騰水で煮沸した牛歯よりダンベル型の試験片を製作し，引張試験を行った．その結果，抜歯直後が76.1 MPaであったのに対し，1週間保管したものでは78.7 MPa，4週間保管したものでは79.9 MPa，1年間保管したものでは79.0 MPaとなった．1年間の冷凍保管では牛歯象牙質の引張強さに変化はみられなかった．一方，牛歯を45分間水中にて煮沸したところその引張強さは，70.3 MPaであり，引張強さは煮沸することによって有意に減少した．

チタン用遠心鋳造による偏析の可能性

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チタン用遠心鋳造機を使用し合金を鋳造する際，凝固過程でのマクロ偏析の可能性について，X線マイクロアナライザーを用いて元素分布マッピング，線分析および定量分析により検討した．鋳込み過程において，溶湯中に局部的に少量の白金が添加されるよう鋳造し，これによる，せいぜい0.1 g/cm^{3}と見積もられた密度差の条件

でも偏析が確認された．この結果は，作用した遠心力の強大なことを裏付けている．しかしながら，チタン合金，Ti-6 Al-4 V を鋳込んだ場合，遠心力によるマクロ偏析は認められなかった．以上の結果より，今回使用した遠心鋳造機では強大な遠心力が発生するが，この合金にマクロ偏析を生じさせることはない，と結論された．

オゾンを利用した可撤性義歯の殺菌

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口腔内には多くの細菌が棲息しているため，可撤性義歯を衛生管理が十分に行われていない状態で，長期間使用しているとデンチャープラークが義歯表面に付着し，義歯性口内炎を起こしたり，義歯特有の臭いを発するようになる．そのため，可撤性義歯を可及的清潔に保つことが重要である．

そこで，われわれは殺菌力，脱臭力に優れたオゾンに着目し，これを義歯の殺菌，洗浄に使用するため，オゾンを使用した義歯洗浄器を試作した．今回はこの試作洗浄器を使用し，デンチャープラークの主体である *Candida albicans* に対する殺菌力を調べた結果，約 10 ppm のオゾン濃度では，30 分後に約 1/10，60 分後に $1/10^3$ 程度に減少することが判明し，可撤性義歯の洗浄に使用可能と思われた．

ヒトおよび動物皮膚に対するデンティンプライマーとしての2種ダイオール水溶液の安全性の評価

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この研究の目的は，当教室で開発されたデンティンプライマーすなわち 62.5%ethylene glycol，45% 1，6-hexanediol 水溶液の皮膚安全性を一次皮膚刺激試験，累積皮膚刺激試験，Guinea Pig Maximization test およびヒトパッチテストによって検討，観察することである．その結果，一次皮膚刺激試験，累積皮膚刺激試験とヒトパッチテストでは両水溶液ともに刺激性は認められなかった．しかしながら，Guinea Pig Maximization test による 2-HEMA に感作された動物に対し，100%hexanediol で弱い誘発反応が認められた．以上の結果より，2-HEMA の様なメタクリル酸プライマーと比較して ethylene glycol や 45% 1，6-hexanediol 水溶液は比較的安全で臨床的にも十分使用可能なプライマーであると思われる．