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Toru Okabe

Baylor College of Dentistry, Dallas

Hakon Hero

Scandinavian Institute of Dental Materials, Haslum

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THE USE OF TITANIUM IN DENTISTRY

Toru Okabe* and Håkon Herø¹

Baylor College of Dentistry, Dallas, TX, USA

¹Scandinavian Institute of Dental Materials (NIOM), Haslum, Norway

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Abstract

The aerospace, energy, and chemical industries have benefitted from favorable applications of titanium and titanium alloys since the 1950's. Only about 15 years ago, researchers began investigating titanium as a material with the potential for various uses in the dental field, mainly because of its proven biocompatibility and other attractive properties. The present review examines updated information on the use of titanium in a major area of dentistry. Titanium-based alloys used for casting, casting equipment and procedures, casting investment materials, and porcelain veneering are discussed. Information about advances made in techniques other than casting, which could widen the applications of this metal to dentistry, is also included.

Key Words: Titanium, dentistry, dental casting, dental prostheses, investment, strength, biocompatibility.

Introduction

Compared to the metals and alloys commonly used for many years for various industrial applications, titanium is a rather "new" metal. Before the success of the Kroll process in 1938, no commercially feasible way to produce pure titanium had been found. The use of titanium alloys has increased since then, mainly because of their good mechanical properties, which include high strength, stiffness, and ductility, along with excellent corrosion resistance (ASM, 1961). The biocompatibility of titanium has been well recognized since 1940 (Bothe *et al.*, 1940; Leventhal, 1951; Clarke and Hickman, 1953), and the explanation for its excellent biocompatibility has recently been reviewed by Hanawa and Ota (1992). Therefore, this metal has long been a highly potential candidate for the manufacture of medical instruments and implants. Williams (1981) stated that titanium is essentially a physiologically indifferent metal and that it seems neither to be an essential dietary element nor to have any significant toxic or irritant effects on tissue. In the 1960's, the first commercial titanium-containing orthopedic implant material was produced in Europe (Lechner, 1991). Titanium and its alloys gradually became materials of great interest to dental researchers, first in the U.S. and then in Japan and Europe. As a result, numerous findings were made in the technology of casting titanium, development of various casting machines, and formulation of special investment materials necessary for preventing the oxidation of titanium.

As early as 1959, Beder and Ploger (1959) suggested how titanium dental castings might be produced using a centrifugal casting machine with induction heating housed in a vacuum chamber and why this would be worth doing. Finally in 1977, at the NIST [National Institute of Standards and Technology (then NBS, the National Bureau of Standards)], Waterstrat (1977) successfully cast experimental partial dental frames using a Ti-Cu (13 wt%)-Ni (4.5 wt%) alloy by melting it in an induction furnace under a reduced atmosphere (approximately 10^{-2} torr). This work was accomplished with the cooperation of the Garrett Corporation, Air Research Manufacturing Company in Arizona. This alloy was

*Address for correspondence:

Toru Okabe
Department of Biomaterials Science
Baylor College of Dentistry
P.O. Box 660677
Dallas, TX 75266-0677

Telephone number: 214-828-8190
FAX number: 214-828-8458

Table 1. Selected mechanical properties for grades 1-4 CP wrought titanium and for types I-IV dental casting gold alloys

Material		0.2% Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	Elastic Modulus (GPa)
CP Titanium	Grade 1	170 ^a	240 ^a	24 ^a	103-107 ^b
	Grade 2	280 ^a	340 ^a	20 ^a	103-107 ^b
	Grade 3	380 ^a	450 ^a	18 ^a	103-107 ^b
	Grade 4	480 ^a	550 ^a	15 ^a	103-107 ^b
Gold Alloys	Type I	100-110 ^c	285-315 ^c	25-30 ^c	77.2 ^d
	Type II	150-185 ^c	315-375 ^c	26-35 ^c	---
	Type III	200-240 ^c	400-450 ^c	30-40 ^c	100 ^d
	Type IV	277-310 ^c	470-520 ^c	30-35 ^c	99.3 ^d

^aNumbers obtained from Donachie (1988, p. 14 and 353).^bNumbers obtained from Boyer *et al.* (1994, p. 178).^cNumbers obtained from Craig (1993, p. 395).^dNumbers obtained from O'Brien (1989).**Table 2.** Impurity limits (wt. %) in unalloyed titanium*.

Designation	N	C	H	O	Fe
ASTM Grade 1	0.03	0.10	0.015	0.18	0.20
ASTM Grade 2	0.03	0.10	0.015	0.25	0.30
ASTM Grade 3	0.05	0.10	0.015	0.35	0.30
ASTM Grade 4	0.05	0.10	0.015	0.40	0.50

*Numbers obtained from Donachie (1988, p. 14).

chosen mainly because of its lower-melting nature [approximate melting temperature: 2,425°F (1,331°C)] which is comparable to that of nickel-chromium alloys (Craig, 1993, p. 426). In this study, a wax pattern was coated using a mixture of yttrium oxide and potassium silicate solution; it was reported that the oxide formed on the surface of the casting appeared to be minimal. After that time, Waterstrat occasionally continued his efforts to examine various factors affecting dental titanium casting in collaboration with Northwestern University researchers (Waterstrat *et al.*, 1978; Waterstrat and Giuseppetti, 1985; Rupp *et al.*, 1987; Mueller *et al.*, 1988, 1990). The group at Northwestern, who had initiated investigations of titanium casting, was headed by Greener (Greener *et al.*, 1986; Taira *et al.*, 1989; Takanashi *et al.*, 1990). At about the same time that Waterstrat performed his work with titanium, Ida's group at Kyoto University, Japan, began experimental casting using the Castmatic machine developed by Okamoto Dental Laboratory and Iwatani and Company, Ltd.

(Takeuchi *et al.*, 1978). His group remained at the forefront of Japanese casting research until studies of dental titanium "exploded" in Japan in the mid-1980's. In Europe, some dental titanium studies, paralleling the research activities in the U.S. and Japan, were performed at various dental laboratories, universities, and other institutions. The first international conference on titanium was organized in 1990 by Weber and Mönkmeyer in Germany. Among the leaders in this activity were Weber's group at the University of Tübingen, a dental clinician, Hruska (in Rome), and other researchers such as Bergman (in Umeå, Sweden), Mönkmeyer (in Frankfurt, Germany), Meyer (in Geneva, Switzerland), and Herø (at NIOM, Norway).

During the last ten years, a tremendous number of research papers have been published on dental titanium; within the last three years, several scientists and research teams have reviewed these topics and presented much information about the application of titanium to dentistry (Waterstrat, 1987; Greener, 1990; Stoll *et al.*, 1991; Pröbster *et al.*, 1991; Lautenschlager and Monaghan, 1992; Hamanaka, 1993; Meyer, 1993; Miyazaki, 1993).

Although some major difficulties still remain, including problems regarding its clinical use (Tani, 1991), the use of titanium and its alloys for dental prostheses holds much promise in the development of materials for dentistry. The present paper focuses on some of these recent developments in dental titanium technology, including developments in titanium-based alloys for casting, casting equipment and methods, investment materials, and porcelain veneering. A summary of the

Table 3. Some properties of titanium before and after casting (from Ida, 1991).

Material	Investment	Tensile Strength (MPa)	Elongation (%)	Vickers Hardness (Hv)
Pure Titanium Grade II				
Before Casting	----	421	25 - 36	137
After Casting	Magnesia	490 - 539	16 - 18	150 - 160
	Phosphate-bonded Silica	510	2	161
Ti-6Al-4V Alloy				
Before Casting	----	1,078	11	264
After Casting	Magnesia	882 - 980	4 - 7	290 - 310

progress made in techniques other than casting, which have widened the applications of this metal to dentistry, is also included.

Dental Applications of Titanium by Casting

Materials for casting

Typical values of yield strength, ultimate tensile strength, elongation, and elastic modulus for the four grades of commercially pure (CP), unalloyed, wrought titanium (99.5%) (ASTM standard) and those for the four different types of dental casting gold alloys are compared in Table 1. When the properties of each grade of CP titanium are compared with each type of gold alloy, it can be seen that CP titanium has similar strength and higher yield strength than each corresponding type of gold alloy. It is also worth noting that CP titanium higher than grade 2 is less ductile than the gold alloys with corresponding numbers. Therefore, unlike dental casting metals, the unalloyed, "pure" form of titanium can be used for fabricating crowns, onlays, bridges, etc. As a result, many titanium casting studies have been initiated with CP titanium. Titanium exhibits an allotropic phase transformation at $882 \pm 2^\circ\text{C}$ (Murray, 1987) in which a hexagonal close-packed (hcp) (α phase) structure is transformed into a body-centered cubic (bcc) structure (β phase) as the temperature is raised above that temperature (Donachie, 1988, p. 28, 133). Even rapid quenching does not suppress the $\beta \rightarrow \alpha$ phase transformation. Thus, a pure titanium casting has an α -hcp structure near room temperature. However, the addition of certain alloying elements to titanium permits the β phase to stabilize; some alloys contain a two-phase ($\alpha + \beta$) structure at room temperature. This two-phase structure allows for more refinement in the casting, and because of its optimal microstructure, an excellent combination of strength and ductility is achieved. The β alloys are in a metastable state which tends to transform to the two-phase equilibrium microstructure. Some β alloys have also been examined for dental applications (Okuno, 1988a) because of their

strength resulting from the intrinsic strength of the β structure (for example, high yield strength) and because of increased malleability attributed to the body-centered cubic structure.

Alpha and near-alpha alloys. The α -phase alloy that has been most commonly examined is commercially pure (CP) titanium. Commercially pure titanium, including near-alpha titanium alloys, generally exhibits the best corrosion resistance. These are also the most weldable of the titanium/titanium alloy family (Donachie, 1988, p. 159, 162). The mechanical properties of α titanium can be altered using different cooling rates after annealing at temperatures higher than that for the $\alpha \rightarrow \beta$ phase transformation; these cooling rates can produce structures with various grain morphologies and therefore produce titanium with varying strengths (Donachie, 1988, p. 162). However, the presence of a minimal amount of interstitial elements such as hydrogen, oxygen, nitrogen, and carbon can affect the mechanical properties in a much more distinct manner. Even a concentration of approximately 0.15 wt% hydrogen produces detectable embrittlement due to the precipitation of titanium hydride when the alloy is slow-cooled in an α -phase region (for example, 400°C). This is why the maximum allowable hydrogen content in each grade of unalloyed titanium is specified in the ASTM standard to be no greater than 0.015 wt% (Table 2). Table 2 lists the allowed impurity limits for each of the unalloyed grades of CP titanium. Small amounts of carbon (up to 0.3 wt%), oxygen (up to 0.8 wt%), and nitrogen (up to 0.4 wt%) all strengthen titanium appreciably but reduce its ductility (Donachie, 1988, p. 159, 162). Thus, as the amounts of oxygen and nitrogen increase, the elongation decreases, as seen in the ASTM standard (Table 2). Note that among these four elements, the allowable amount of hydrogen is one order of magnitude lower, indicating the importance of controlling the hydrogen concentration. Even aging titanium with 100 ppm hydrogen at 25°C (77°F) was reported to cause embrittlement (Donachie, 1988, p. 162). Also note that the amount of iron is specified in each grade of titanium

Table 4. Selected properties of some cast dental alloys (from Okuno and Hamanaka, 1989).

Alloy	Casting Investment	Mold Temp. (°C)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Elastic modulus (GPa)	Resilience (J/m ³)	Hardness (Hv)
Ti (Grade 1)	Magnesia	R.T.	277	347	43.5	104	0.37	115
		800	286	354	29.0	114	0.36	129
Ti-Cr-Si	Phosphate-bonded Silica	R.T.	809	938	14.5	110	2.79	320
		800	669	874	5.6	111	2.02	318
Ti-Pd-Cr	Phosphate-bonded Silica	R.T.	680	850	10.3	109	2.12	263
		800	659	880	5.0	107	2.03	261
Co-Cr			710	870	1.6	224	1.13	432
Ni-Cr			690	800	3.8	182	1.31	300
Gold Alloy Type IV			493	776	7.0	90	1.35	264

because the oxygen and iron contents principally determine the strength level of CP titanium. An important fact about these impurities is that the mechanical properties of titanium after casting often deviate from what is observed in pure CP titanium ingots before casting (Table 3) (Ida, 1986): tensile strength and hardness frequently increase, whereas elongation significantly decreases to a degree that is dependent on the types of casting machine, crucible, and investment material used. Thus far, it has been explained that these changes in properties after casting were attributed to the incorporation of oxygen during the melting and casting processes (Ida, 1986). In Table 3, it can be seen that a similar trend has also been observed for the titanium alloy Ti-6Al-4V. Therefore, casting needs to be performed under very precisely controlled conditions.

Unalloyed titanium is not the only form of titanium consisting solely of α -phase grains. When titanium alloys contain elements which stabilize the α phase, the maximum temperature at which the α phase is stable increases. Therefore, the binary α or near- α alloy has a phase diagram of a simple peritectic or a peritectoid system as classified by Molchanora (Collings, 1988). Some common α -stabilizing elements are aluminum, oxygen, nitrogen, carbon and boron. Some α or near- α titanium alloys have been examined for use in dental castings by several investigators (Waterstrat, 1977; Ida *et al.*, 1983; Okuno *et al.*, 1985; Taira *et al.*, 1989); the alloy systems investigated included Ti-Ag (up to 50 wt%), Ti-Cu (up to 30 wt%), and Ti-13Cu-4.5 Ni. The addition of copper to titanium is not recommended since the alloys are brittle (probably due to the precipitation of Ti₂Cu), although copper is considerably more effective in reducing the liquidus temperature (Okuno *et al.*, 1985). In contrast to copper, the addition of silver did not make alloys brittle, and some ductility was maintained.

Beta alloys (metastable beta alloys). Alloying titanium with beta stabilizers results in the stability of the beta phase at lower temperatures. The phase diagrams of beta alloys usually have partial miscibility in the α and β phases and eutectoid decomposition of the β phase. Many elements, including: Au, Ag, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, Pd, Si, Ta, V, and W, exhibit this beta-stabilizing effect when alloyed with titanium (Collings, 1988; Okuno, 1988a). None of the elements is able to form 100% pure β phase at room temperature; however, in some of the alloy combinations, a metastable β phase may be retained since the $\beta \rightarrow \alpha$ transformation in these alloys is usually slow. Cold working at ambient temperatures or heating to elevated temperatures can cause partial transformation of the β phase to the α phase. In general, one advantage of the β phase alloys is that they have lower fusion temperatures since the solubility of alloying elements is often extensive (Okuno, 1988a); they can be strengthened, if needed, by solution heat treatment. These alloys have excellent forgeability at elevated temperatures and good cold-formability because of their crystal structure (bcc). These mechanical properties indicate that the β titanium alloys seem to be excellent candidates for dental casting alloys. Systematic work on binary β titanium alloys was initiated by Okuno *et al.* (1985) and Okuno and Hamanaka (1989). They examined various binary and ternary titanium alloys employing Co, Cr, Fe, Mn, Pd, and Si as β stabilizers. They suggested that Ti-20Cr-0.2Si and Ti-25Pd-5Cr would be well suited for casting fixed bridges, clasps, and denture frameworks for removable prosthodontics, as can be seen in the comparison of the mechanical properties of these alloys with those of the type IV gold alloys (Table 4). Another β titanium alloy, the Ti-V (15%) alloy, was investigated by Taira *et al.* (1989). Castings made using this alloy and a phosphate

investment with a Y_2O_3 or Zr_2O_3 coating technique showed high tensile strength (~ 1000 MPa) with only 1.7% elongation. No report appears to have been published with respect to the castability and corrosion resistance of these alloys mentioned above.

Alpha-beta alloys. The addition of enough β stabilizer to titanium results in the formation of $\alpha + \beta$ phase structures. These alloys retain a hard β phase in the relatively soft α phase precipitated during cooling; the specific amount of these phases depends on the type and quantity of β stabilizers present and on the heat treatment. The result is an alloy of high strength in which formability is not sacrificed. One of the most successful α - β alloys is Ti-6Al-4V, which has an excellent combination of strength, toughness, and corrosion resistance (Donachie, 1988, p. 31). This alloy has been popular for various industrial uses including aerospace applications, aircraft turbines, compressor blades and disks. Aluminum is one of the α stabilizers which increase strength without reducing elongation and toughness when alloyed to a maximum of 6 wt% titanium; the addition of vanadium contributes solid-solution strengthening of the β phase and the capability of solution treating and aging in the α - β region (Okuno, 1988a). Some investigators have examined this alloy for use in various dental applications. When cast, using an investment casting technique similar to the one that Taira *et al.* (1989) used for the β Ti-V alloy casting, the Ti-6Al-4V alloy exhibited properties similar to the Ti-V alloy (Okuno, 1988a). Okuno (1988a) found that the cast Ti-6Al-4V alloy had significantly higher strength but lower ductility compared to a wrought form of the alloy as reported by Ida (1986) (Table 3). Considering the excellent strength obtained, Okuno (1988b) suggested that this alloy could be used for fabricating partial denture frameworks and even complete cast denture bases.

Cast appliances made from an alloy such as Ti-6Al-4V are strong enough for dental prosthodontic applications, and therefore, it may not be necessary to further strengthen the alloy for dental applications. However, for fabricating complete denture bases and multiple-unit bridges where greater strength is required, the heat treatment processes may become important, depending on the titanium alloy systems used in dental titanium casting. Also, careful consideration must be given to the structural changes of the titanium alloys in case a ceramic coating is applied at a high temperature. In using a titanium alloy, one should keep in mind that important differences in the behavior of molten metal exist between the pure state of titanium and a titanium alloy. For instance, the addition of alloying elements to a pure metal always decreases "fluidity" and therefore, castability. According to Flemings (1974), this is because solidification no longer takes place with a planar surface. The dendrites that form create more resistance to fluid flow at an earlier stage of solidification. Although this

statement is only true if the same casting conditions are used for both metals, careful examination is needed when selecting an alloy system for titanium casting.

Casting machines

Because of the inherent properties of titanium that made it difficult to melt and cast this metal, traditional dental casting machines that cast in air with conventional ceramic crucibles and investment materials could not be used; more specialized casting equipment and mold materials developed solely for this purpose were required. Casting problems arose from several factors: the high melting point of titanium (1670°C, Murray, 1987); the strong chemical affinity of titanium with gases such as oxygen, hydrogen, and nitrogen; the high reducing ability of titanium; the unusually high solubility of some gases (oxygen, for example) in titanium; and the relative low density of titanium. Therefore, improvements in conventional dental casting methods were required to overcome these problems. From the many innovative ideas which have evolved in the titanium industry over the last 30 years, some important features introduced for dental titanium casting were: selecting heat sources high enough for fusing titanium; isolating the molten metal from air; developing a container which reacts very little or does not react at all with the molten titanium; and finding new ideas for delivering the molten metal into the mold at the desired velocity.

More than ten different casting machines for dental titanium alloys are currently available on the market. These machines can be classified according to the melting methods and the casting processes they use (Hamanaka, 1993). In all of them, melting is performed under an inert gas (usually argon because of its price) in order for the highly reactive titanium melt not to react and "absorb" oxygen and nitrogen from the atmosphere. To reach the high melting point of titanium, electric arc melting or high-frequency induction melting methods are used. In order to pour the molten metal into the mold during the casting process, either a differential gas pressure mode or centrifugal force casting is employed. By combining these melting and casting techniques, four different types of machines have been developed. Table 5 lists representative commercial casting machines which correspond to each of the four different operating modes. Crucibles made of copper (in the Autocast, Castmatic, Cyclarc, and Tycast 3000), ceramic (in the Titaniumer, Argoncaster, and Arvatron) or carbon (in the Ticaster) are used to contain the molten titanium alloys. A detailed explanation of the Tycast 3000 (Brodersen and Prasad, 1992) is given in articles such as ones by Prasad *et al.* (1994) and Takanashi (1993).

In the electric arc/gas pressure casting equipment (such as the Castmatic), the equipment consists of two chambers: (1) an upper melting chamber which houses a copper crucible and a tungsten electrode [in a more recent Castmatic model, an improved copper crucible

Table 5. Titanium Casting Systems

Melting	Casting		Equipment	
Electric Arc	Gas Pressure	Castmatic	Iwatani (Osaka, Japan)	
		Cyclarc	Morita (Tokyo, Japan)	
		Autocast	GC (Tokyo, Japan)	
		Super Caster	Ikura Seiki (Japan)	
	Centrifugal Force		Titaniumer	Ohara (Osaka, Japan)
			Ticast	Kobelco (Kobe, Japan)
		Tycast 3000	Jeneric/Pentron (Wallingford, CT, USA)	
High Frequency Induction	Gas Pressure	Arvatron	Asahi Roentgen (Kyoto, Japan)	
		Vulcan-T	Shofu (Kyoto, Japan)	
	Centrifugal Force		Titanus	Bego (Bremen, Germany)
			Vacutherm	Linn (Hirschbach, Germany)
			Centrivac	Cowa (Dusseldorf, Germany)

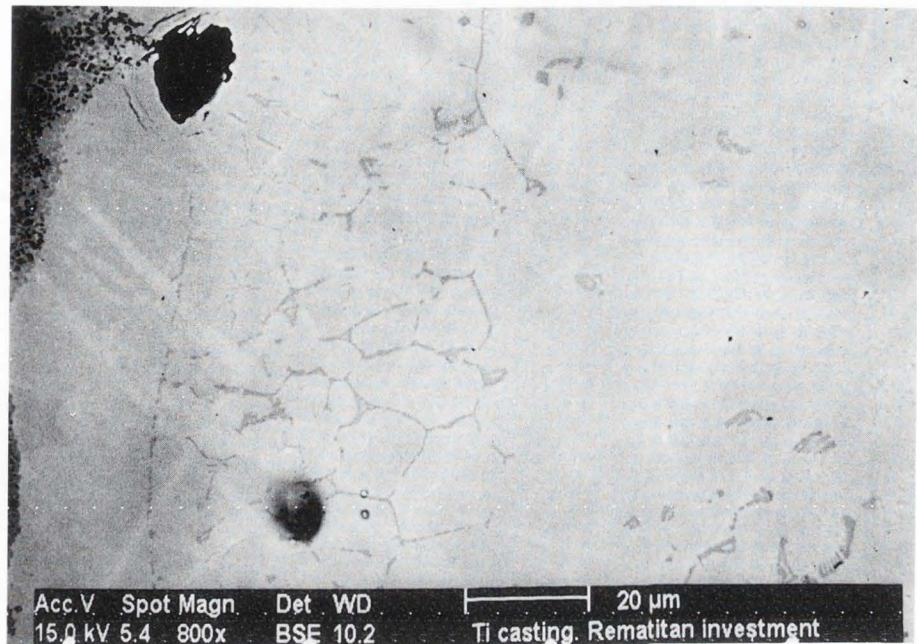
with tilting capacity is used (Hamanaka, 1993)], and (2) a lower casting chamber connected to the upper chamber by placing the invested mold so that the opening in the mold matches the opening at the center of the copper crucible. After placing the piece of titanium ingot to be melted in the crucible, both chambers are evacuated, and argon gas is then introduced into the melting chamber. The pressure of the argon in the upper chamber is adjusted, and heating is initiated with the argon arc generated between the titanium piece and the non-consumable tungsten electrode aligned at the center of the titanium piece; the titanium is then arc-melted at a temperature which is reported to be as high as 6000°C (Hamanaka, 1993). Melting begins immediately, and one end of the molten metal moves toward the bottom of the ingot. Because of the low thermal conductivity of titanium [0.02-0.43 cal/cm²/cm/°C/sec for titanium or titanium alloys versus approximately 0.94 for pure copper (ASM, 1985)], a considerable amount of thermal energy is retained at the center of the titanium piece within a limited time, usually approximately 60 seconds, until the molten metal suddenly drops down into the mold. During the melting or the pouring stage of the operation, the molten metal touches the surface of the copper crucible and immediately solidifies at the crucible surface; the crucible acts as a heat sink due to its large mass compared to the piece of titanium and also due to the high thermal conductivity of copper. As a result, a large part of the molten metal flows on the titanium layer solidified on the crucible into the mold without any appreciable contamination. This is called "skull melting" and has been used for a long time for melting high-temperature alloys (Boyer *et al.*, 1994, p. 1079). The Castmatic casting machine is a down-scaled version of the typical arc melting/casting equipment which was developed earlier in the

U.S. for the industrial casting of titanium and its alloys. This machine has been used ever since with occasional modifications. Some investigators have examined home-made equipment of this type (Sunnkrantz *et al.*, 1990).

Machines such as Cyclarc, Autocast, and Super Caster adopted the same basic type of melting and casting methods as in the Castmatic. Each machine possesses different elaborate innovations. Details of the differences in each machine are given elsewhere (Togaya and Tani, 1989; Miyazaki, 1990; Hamanaka, 1993). Among the differences, one notable aspect is the design of the crucible. Many machines now use a copper crucible with the capability of tilting or splitting in two when pouring the molten titanium; this capability allows the mass of titanium to drop in a more controlled manner. Each type of crucible has advantages and disadvantages. The free-falling system that the original Castmatic used is good since overheating of the molten metal can be avoided. In contrast, in other types of crucibles, superheating of the melt is possible when needed. A significant disadvantage of the arc-melting system is that the temperature during the melting process is very difficult to record and control. Better control of the temperature, including superheating, can be found in a system using high-frequency induction heating.

The Titaniumer, Ticast, and Tycast 3000 casting machines utilize an electric arc for melting and centrifugal force for casting. In this system, the parts for melting and casting are housed in one chamber. Before melting, the chamber is evacuated and then filled with argon gas. Instead of using a copper crucible, the Titaniumer uses one made of magnesia, while the Ticast uses a carbon crucible. Even though more stable materials are used in the crucibles, extreme caution may be needed to avoid contamination of the molten metal by

Figure 1. A cross-sectional area near the surface of cast unalloyed titanium: some precipitated phases which contain silicon and phosphorous are seen along the grain boundaries of the casting (Herø, work in progress).



the crucible materials. The Tycast 3000 uses a copper crucible as is used in the Castmatic. Because the density of titanium is low, new ideas were needed for pouring the molten titanium into the mold at high velocity when the centrifugal casting method was used. The Titacast is equipped with a special motor-driven casting turntable that spins at approximately 3000 rpm (Meyer, 1993). The metal is melted by the arc and is poured through the opening at the center of the casting table. Since the casting table is rotated at high velocity prior to casting, the molten metal reaches the mold within 0.02 seconds at an acceleration of more than 200 times the force of gravity (Stoll *et al.*, 1991). This method is called "spin casting" (Togaya, 1990). It is reported that a large casting can be made without appreciable defects (Togaya, 1990).

In melting a metal in a high-frequency induction furnace, a crucible with no electrical conductivity should be used. Therefore, in the Arvatron and Argoncaster machines, which use induction melting instead of arc melting, the metal must be melted in a ceramic crucible. The Argoncaster uses a crucible made of calcia while in the Arvatron, the calcia or magnesia crucible is connected on the top of the mold as a single body. Since the chemical stability of these ceramics at the operating temperature of the casting machine is considered to be greater than that of the various titanium oxides (shown later in Figure 2), it has been reported that the titanium can be melted without contamination from the crucible material (Miyazaki, 1990). The casting force is created from the differences in the gas pressure as in the other machines discussed above.

Among the machines belonging to the last type of operation are the Titanus, Vacutherm, and Centrivac,

which utilize centrifugal force for pouring the molten metal after induction melting. The casting turntable of the Titanus is reported to be operated at the same speed as that employed in the Titacast described above. The reaction between the metal and the mold is minimized since a specially made ceramic crucible is used. Impurities are found only in the fins of the casting (Stoll *et al.*, 1991).

Investment materials

Even if an ideal titanium alloy system is available and a casting machine is developed which meets all the necessary requirements for the production of titanium castings for dental use, an acceptable titanium dental appliance cannot be made without using a mold material specifically developed for this purpose. While pioneering titanium casting technology in Japan at the end of the 1970's, the staff of Dr. Ida's research team at Kyoto University used a conventional silica-based, phosphate-bonded investment for casting pure titanium (Ida, 1991). They found that the molten metal reacted upon solidification with the investment material, the investment adhered tightly to the surface of the casting, and some areas of the cast titanium surfaces cracked. They also found that the surface of the titanium hardened.

This hardened layer is known in the titanium casting industry as the "alpha case" (Donachie, 1988, p. 69, 71) since oxygen (and sometimes nitrogen) reacts with the titanium at its surface; oxygen and nitrogen are α stabilizers. This has also been a common problem during heat treatment in air at high temperatures. The alpha case is detrimental because of the brittle nature of the structure, giving the metal reduced ductility as well as reduced fatigue resistance (Donachie, 1988, p. 28; Miyakawa *et*

Table 6. Commercially Available Investment Materials for Dental Titanium Casting (Togaya, 1993).

Type	Investment Material	Main Refractory	Binder
SiO ₂ -based	Rematitan (Dentaurum, Newton, PA, USA)	SiO ₂ , Al ₂ O ₃	MgO, Phosphate
	Titanvest (Denco, Tokyo, Japan)	ZrSiO ₄ , SiO ₂	MgO, Phosphate
	Tancovest (Bego, Bremen, Germany)	SiO ₂ , Al ₂ O ₃	MgO, Phosphate
Al ₂ O ₃ -based	Titaniumvest EX (Ohara, Osaka, Japan)	Al ₂ O ₃ , ZrO ₂	MgO, Phosphate
	Titan supermild (Ohara)	Al ₂ O ₃ , SiO ₂	MgO, Phosphate
	Titan crown master (Ohara)	Al ₂ O ₃ , ZrO ₂	MgO, Phosphate
	Titanmold (Yoshida, Tokyo, Japan)	Al ₂ O ₃ , ZrO ₂	MgO, Phosphate
	T-investment (GC, Tokyo, Japan)	Al ₂ O ₃ + LiAlSiO ₆	MgO, Phosphate
MgO-based	Titavest PS (Morita, Tokyo, Japan)	MgO, Al ₂ O ₃	Ethylsilicate
	Titavest PP (Morita)	MgO, SiO ₂ , Al ₂ O ₃	Ethylsilicate
	Titavest CB (Morita)	MgO, Al ₂ O ₃	Cement (?)
	Titavest ME (Morita)	MgO, Al ₂ O ₃	Cement (?)
	Titavest MZ (Morita)	MgO, Al ₂ O ₃	Cement (?)
	Cerevest D (Nissin, Kyoto, Japan)	MgO	Alumina cement
	Selevest DM (Nissin)	MgO + Zr powder	Ethylsilicate
	Selevest DM(W) (Nissin)	MgO + Zr powder	Alumina cement
	Selevest CB (Nissin)	MgO + Zr powder	Alumina cement

al., 1991). A more recent study of the alpha case formed on a titanium casting using a phosphate-bonded SiO₂/Al₂O₃ investment revealed the existence of oxygen, aluminum, and carbon within the hardened layer besides the presence of silicon and phosphorous (Miyakawa *et al.*, 1989). A similar accumulation of silicon and phosphorous near the surface layer was found when pure titanium was cast into a mold made by Rematitan (Dentaurum, Germany) at room temperature (Fig. 1). A cross section of the casting showed the formation of phase(s) containing a concentration of 5 wt% each of silicon and phosphorous which was detected using an X-ray energy dispersive analyzer (Herø, 1994, work in progress). Okuno *et al.* (1987) determined the concentration profile for oxygen in the hardened layer of the cast titanium. Another detrimental effect of this hardened layer is the interference in the bonding of titanium to porcelain (Hautaniemi *et al.*, 1993); this is described in the forthcoming section on **Porcelain veneering**. Since the surface quality crucially affects various processes which follow the casting procedure and also the cost of the whole process, examination of the surface has been one of the more active areas of research (Hashimoto *et al.*, 1992; Zhang *et al.*, 1994).

Among the compounds in regular investment materials, the interactions of SiO₂ and various phosphate species appear to be the most severe with the molten titanium. This can be understood from the comparison of

the standard free energies of formation of various oxides as a function of temperature [see Figure 2 which was constructed using the data in Kubaschewski and Alcock (1979)]. At equilibrium near the melting point of titanium (~ 1700°C), all the titanium oxides appear to be more chemically stable than SiO₂; this explains why the molten pure titanium readily reduces SiO₂ (Togaya, 1986). Therefore, oxides whose standard free energies of formation have a greater negative value than that of titanium oxide up to a temperature near the melting point of titanium could possibly be used as the refractory materials in the investment material. As seen in Figure 2, these oxides are Al₂O₃, MgO, ZrO₂, CaO, BeO, and Y₂O₃.

Since the early 1980's, the development of a workable investment for the dental casting of titanium has continued in an effort to fulfill the requirements such an investment must meet. Necessary requirements are adequate strength at room temperature as well as at elevated temperatures, ease of handling, smooth surface, a relatively short setting time, and low cost. Additional characteristics desired for a dental casting investment are: (1) chemical stability at high casting temperatures; (2) adequate expansion to compensate for the shrinkage of the metal; and (3) permeability that permits air or other gases in the mold cavity to escape easily during the casting process. The importance of the first desired requirement has been discussed. To fulfill the second

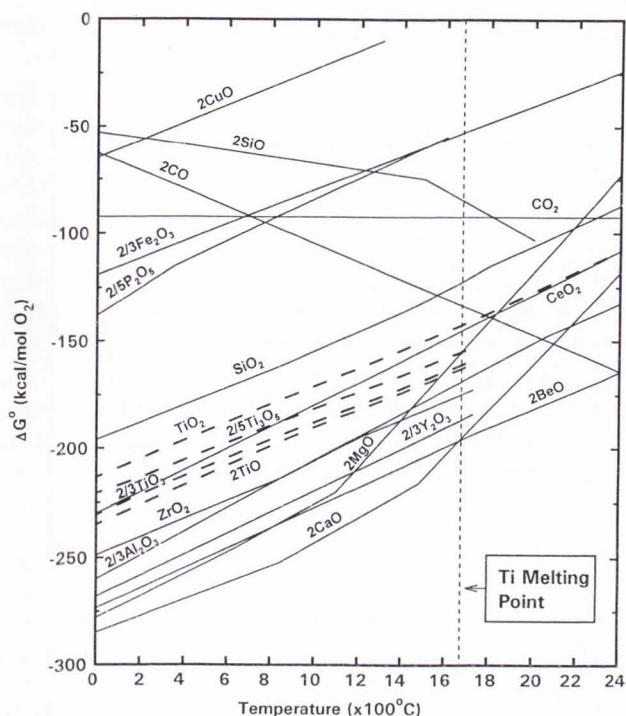


Figure 2. Standard free energy of formation for titanium oxides and other oxides (from Kubaschewski and Alcock, 1979).

requirement, new ideas are needed to expand the investment when silica is not used as the refractory component of the investment. The third desired requirement is crucial because, when the compressive force on the melt in the mold is limited, trapped argon in a mold with low gas permeability creates a substantial back pressure which may prevent complete filling of the mold.

Much research has been performed in Japan and Europe on developing an investment for dental titanium casting; several different ideas have been proposed and tested. As of the end of 1993, more than 15 different investment materials were being marketed. If these materials are classified based on the main refractory materials they contain (Togaya, 1993), these investments can be divided into three different groups: silica-, alumina-, and magnesia-based materials (Table 6). Table 6 lists the commercial products and also the principal binder used for each refractory material.

A silica-based material should not be used since the desired qualities of the casting are reduced, as previously noted. However, the combination of silica as a refractory and some phosphate species as a binder is feasible because of the thermal expansion by the polymorphic transition of silica (quartz or cristobalite) from the α to β form and the quick setting of the phosphate binder which supplies the high strength of the investment after the burn-out process; an added advantage of this combi-

nation is its economical price.

Various attempts have been made to improve the silica/phosphate investment by altering the component compounds with different additives, mainly because of the desirable properties that these materials have. One suggestion for using this type of investment material is to select a lower mold temperature (room temperature-600°C) so that the risk of oxidizing the titanium in contact with the investment is minimized. However, there is always the danger of contaminating the titanium with phosphorus, which introduces surface irregularities and degrades properties. A better choice of investment seems to be either an alumina-based or a magnesia-based material. Since either of these oxides has a greater negative value for free energy of formation than that of the titanium oxides (Fig. 2), the reaction between the molten metal and these investment materials is diminished, compared to the reaction expected with the silica-based materials.

Since alumina- or magnesia-based investments usually do not contain silica (Togaya, 1993), their casting shrinkage has to be compensated for through mechanisms other than the α - β transition of the SiO_2 material. A few solutions have been proposed: the first is to utilize irreversible expansion when a spinel compound ($\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgO} \cdot \text{Al}_2\text{O}_3$) is formed at 900-1200°C, depending on the investment. The change of expansion as a function of temperature for a $\text{MgO}/\text{Al}_2\text{O}_3$ -based investment (Titavest CB) is given in Figure 3 (Tanaka, 1993). The second method for managing thermal expansion is to use the compound, $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (spodumene), which expands at 1050°C due to a phase change (Okuda, 1993). When this type of experimental investment is used, an elongation of 23% of the cast unalloyed titanium occurs, and the margins of the crowns are pliable for the necessary burnishing (Meyer, 1993). Another method mixes metallic powder into the body of the investment and makes use of the irreversible thermal expansion which occurs during the oxidation of the powder in the heating process. Figure 4 (Togaya, 1993) compares the expansion curve of a magnesia-based investment material during heating with and without the inclusion of metallic zirconium powder. With the oxidation of zirconium ($\text{Zr} + \text{O}_2 \rightarrow \text{ZrO}_2$), the magnesia-based investment exhibits irreversible thermal expansion (Togaya *et al.*, 1985). Since ZrO_2 is more stable than titanium oxides, no reaction with the molten titanium is expected. Togaya *et al.* (1981) reported that a total expansion of 2.0% can readily be achieved by adding the appropriate amount of zirconium powder necessary to obtain an acceptable fit of the experimental crowns.

In addition to the materials discussed above, there are other materials that can be used as investments (Nakamura, 1988; Togaya, 1993); many of them are at the experimental stage and are not ready for commercial use. These include zirconia-, calcia- and yttria-based

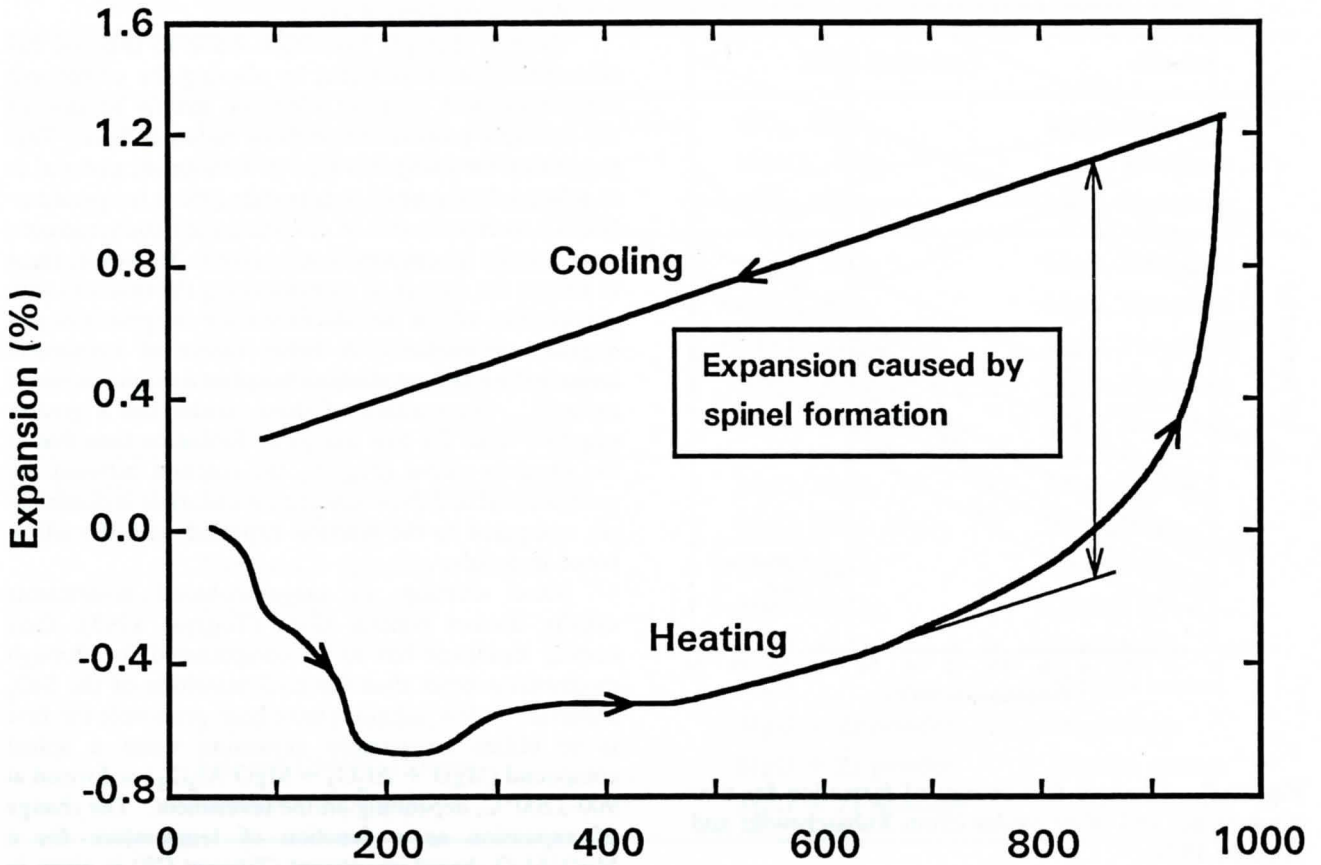


Figure 3. Investment expansion by formation of a spinel compound ($\text{MgO}\cdot\text{Al}_2\text{O}_3$) (Togaya, 1993).

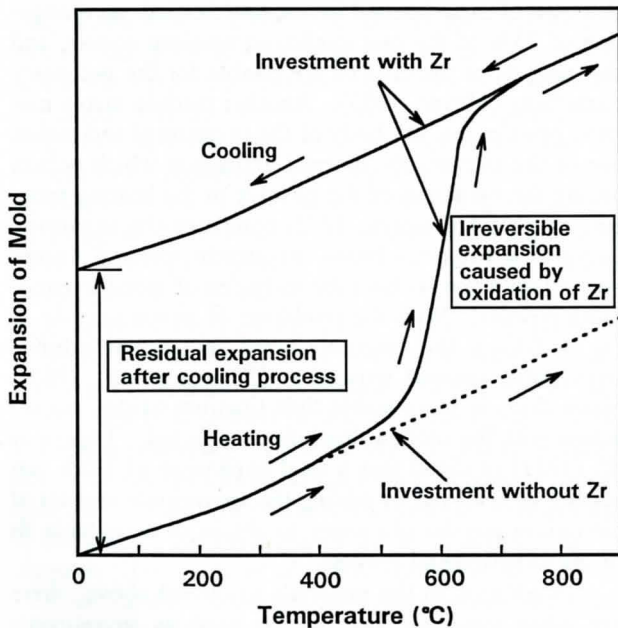


Figure 4. Thermal expansion of MgO-based investment with or without Zr powder during heating and cooling processes (Togaya, 1993).

materials. Some of them are more chemically stable than others, but are more expensive, so these materials are often used in a coating technique. In this method, a wax pattern is coated with a few millimeters thick layer of a chemically stable oxide like ZrO_2 . The coated wax pattern is invested with a less expensive material. This method reduces the cost and, at the same time, reduces the reaction between the titanium and the investment during casting. However, this type of method is more time consuming and requires more labor.

Two different mold temperature ranges for casting are suggested, depending on the components of the investment: these ranges are $100^\circ\text{-}200^\circ\text{C}$ and $600^\circ\text{-}700^\circ\text{C}$ (Togaya, 1993). In general, within practical limits, the higher the mold temperature, the lower the cooling rate of the melt. This increases the possibility of completely filling the mold. On the other hand, the lower the temperature of the mold, the less the reaction which takes place between the metal melt and the investment materials, possibly resulting in less adherence, a cleaner and smoother casting surface, and less contamination near the surface of the casting. In addition, when the temperature is lower, the molten titanium solidifies more rapidly, decreasing the possibility of contaminating the surface of the casting by the oxygen and nitrogen that exist in the mold structure and the mold cavity.

Problems associated with casting

Despite the numerous research and development efforts in titanium dental casting technology, there still remain some major problems in presenting titanium as a new material to add to the already established group of noble and base metals dental alloys in use in prosthetic dentistry. The main problems in the current level of dental titanium casting are presented here by concentrating on the following three areas: (a) surface quality; (b) incomplete casting; and (c) internal porosity.

Surface quality. One of the most important factors for obtaining a casting with a smooth surface and minimized reaction is the investment material. Ignoring factors such as the price of the investment and ease of use, it is possible to obtain cast titanium with a metallic luster even without sand-blasting. However, a hardened layer of at least 50-100 μm thickness forms on the surface of even the best examples of casting which can be produced using currently available casting machines and investments (Togaya, 1986). Figures 5 and 6 demonstrate how the selection of the investment material affects the surface quality of the titanium made by casting (Okuno, 1994, personal communication). In Figure 5, a cross section of the fracture surface of unalloyed titanium, broken in tensile testing, is shown. This specimen was cast into a phosphate-bonded silica-based investment at room temperature. The scanning electron micrograph in Figure 6 shows the area near the surface of the specimen (identified by a rectangle in Fig. 5). Figure 6 suggests that the fracture process occurred through two different modes: a brittle fracture near the surface where the river patterns are observed; and a ductile fracture in the interior of the cross section identified by the presence of dimples. Note that the thickness of the brittle layer is as much as 300 μm . On the other hand, Figure 6 was obtained from a fractured unalloyed titanium specimen cast at 800°C in a magnesia-based investment material. In this figure, the reaction-affected, hardened layer appears to be approximately 100 μm thick and does not seem to be continuous around the circumference. Certainly, the thickness and extent of the reaction layer decreased when the titanium was cast using the recommended investment. The mold temperature also seems to be an important factor in minimizing the formation of the alpha case. In any event, since the hardened layer must be removed to fabricate better crowns and inlays, the size of the wax pattern and/or thermal volume changes in the investment mold must take into account this removal of the surface layers. When making a partial denture framework and complete denture base, the dimensional requirements become less severe (Stoll *et al.*, 1991).

Since it is expected that using a better vacuum will minimize the contamination of the casting by residual gases, Yoneyama *et al.* (1990) cast unalloyed titanium using a phosphate-bonded investment at 800°C under

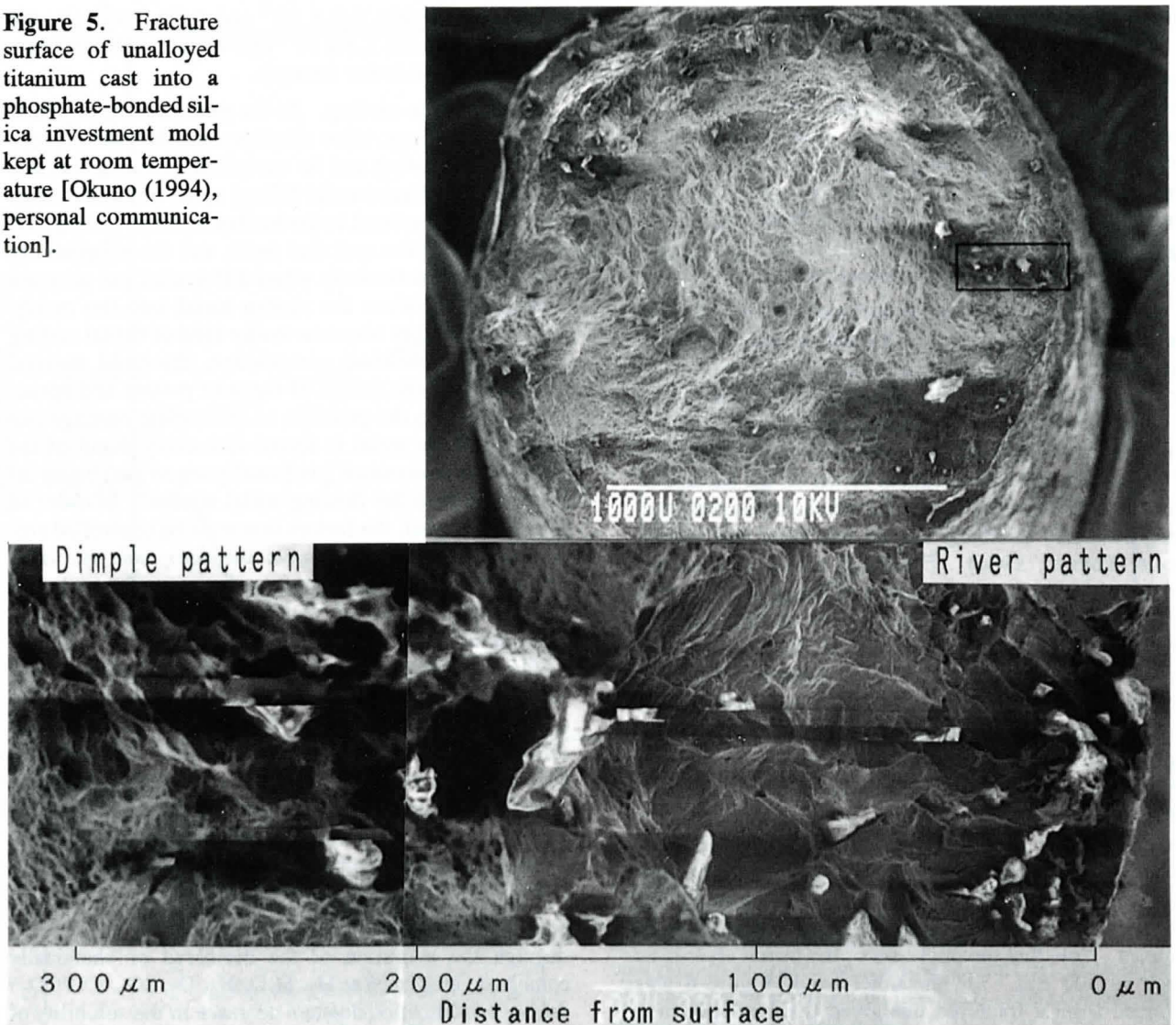
two vacuum levels: 2.0×10^{-1} and 1.5×10^{-4} torr; the specimen from the 1.5×10^{-4} torr vacuum exhibited better ductility and lower strength.

Incomplete casting. At the present level of dental casting technology, close attention must be paid to preparations for casting and its execution. Among the factors which influence mold filling, some prominent ones are the force rendered to the molten metal in casting, the temperature of the melt and mold, and the permeability of the mold (particularly when differential gas pressure is used to introduce the molten metal into the mold). Additional factors common to any kind of dental casting are the alloy chemical composition, the mold material selection, and the design of the wax pattern and sprue. The solution to the problem of incomplete castings lies in how fast the metal is forced into every detail of the mold without too much gas (usually argon gas) being incorporated into the flowing metal stream. In order to achieve this goal, the factors that must be controlled are: the appropriate casting force; the equipment (utilizing either differential gas pressure or centrifugal force); and an investment material with the desired permeability. Herø *et al.* (1993a) produced a good example of cast unalloyed titanium which incompletely filled the mold for a five-unit, simulated fixed partial denture. The casting was made in a low permeability mold using a differential gas pressure casting machine. When an investment with a high enough permeability was used, the mold was completely filled. These results indicate that the adjustment of the mold permeability was crucial to obtaining a sound, complete casting.

Internal porosity. In casting with metals other than titanium, a majority of the internal pores are created through the evolution of the dissolved or chemically combined gases (such as H_2 , H_2O , N_2 , O_2 , SO_2 , CO/CO_2) during solidification due to a decrease in the solubility of gas and decreasing temperature. Alternatively, these pores can exist near an area which undergoes the last stage of the solidification process (Flemings, 1974; Okuno, 1991).

The mechanism of internal porosity formation in dental titanium casting is not quite the same as void formation in the casting of conventional metals because: (1) the solubility of gases such as oxygen, nitrogen, and hydrogen in the molten titanium is unusually high (approximately 15 wt% O and 2.5 wt% N at 800°C, and 0.2 wt% H at 500°C) (Murray, 1987); and (2) the titanium melt very quickly solidifies in a volume with thin cross sections in dental appliances because of the large temperature difference between the molten titanium and the mold. The surfaces of the internal pores exposed on the fracture surface of a dental titanium casting often have a metallic luster (Okuno, 1991). According to Okuno (1991), high internal porosity in the titanium casting occurs for several reasons: (1) when the suctioning pressure is too high because of a large pressure difference

Figure 5. Fracture surface of unalloyed titanium cast into a phosphate-bonded silica investment mold kept at room temperature [Okuno (1994), personal communication].

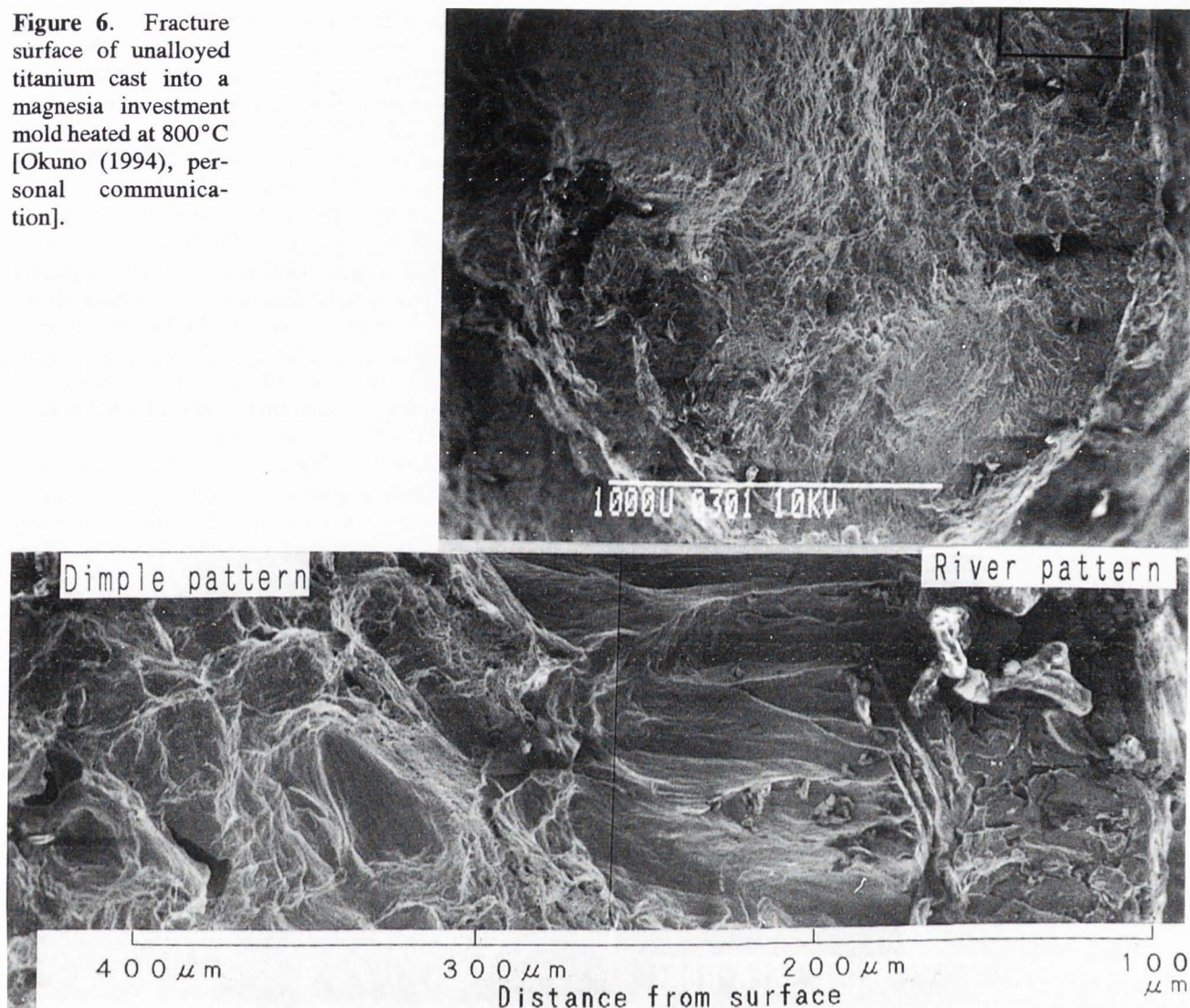


between the casting chamber and the mold chamber, gas (argon gas) is introduced into the flowing melt; (2) if the speed of the flowing molten metal is too fast, severe turbulence can be produced in the metal stream which then results in gas incorporation; and (3) when the wettability of the surface of the mold to the molten titanium is too great, the metal flow becomes intermittent; the metal poured first travels too quickly to the end of the mold, immediately solidifying, and the metal following the first pour flows less rapidly. Using X-ray radiography, Herø *et al.* (1993b) showed that, even though the outside appearance of the five-unit unalloyed titanium bridge seems to indicate perfect casting, numerous pores can be found in the interior of the casting when the difference in the pressures in the two chambers is too high (400 torr) despite the use of separating foil. However, when castings were made under argon pressure of 50 torr in similar conditions, almost no porosity was found.

Clinical applications of cast titanium

Several investigators have examined the clinical performance of cast titanium restorations. In 1987, a group at NIST reported that cast titanium crowns met some of the necessary criteria for clinical use (Rupp *et al.*, 1987). Tani (1991) reported the results of a clinical trial of crowns (28 units) and inlays (14 units) between 3 and 6 years which he started in 1982. He reported that the results from all patients were satisfactory except for three patients whose teeth restored with titanium were fractured. Titanium cast crowns having sufficiently smooth surfaces retained their luster better than crowns made with Au-Ag-Pd alloys or Ni-Cr base-metal alloys. As for the fit of titanium cast crowns and inlays, qualitative examination by Tani suggested that the precision of titanium prostheses was moderately inferior to that of noble alloy prostheses but far superior to the fit of Ni-Cr alloy prostheses. Kawazoe (1992) also evaluated more

Figure 6. Fracture surface of unalloyed titanium cast into a magnesia investment mold heated at 800°C [Okuno (1994), personal communication].



than 100 cases of cast titanium crowns, and the results are consistent with Tani's study. Kawazoe (1990) further reported that the fit of the crowns was found to be 40-80 μm and 150-200 μm at the axial and occlusal surfaces, respectively. In these studies, no discoloration of the restorations was reported. However, Tani indicated that titanium requires more time to finish and polish compared to Au-Ag-Pd and Ni-Cr alloys and that the color of the titanium is "darker", despite being glossy. Patients using titanium prostheses reported a negligible metallic taste. Also, Tani observed that plaque formation on the surface of the titanium crowns does not appear to differ from that of alloy crowns. Vitik (1991) reported similar clinical findings. On the other hand, Pröbster *et al.* (1991) published results indicating that titanium restorations have a tendency to form plaque and calculus on their surfaces. Further studies, including both *in vitro* and clinical studies, are needed before we

will know if there is any difference in the deposit and removal of adhered plaque and tartar.

In a more recent *in vitro* determination of marginal fit, Rappo (1994) reported the results of 20 cast titanium copings to be $23 \pm 5 \mu\text{m}$ and $52 \pm 9 \mu\text{m}$ for coronal adaptation and marginal adaptation, respectively. These results are comparable to those obtained by Herø *et al.* (1990) who reported that the space between the tooth abutment and inner surfaces of pure titanium crowns was 30-50 μm .

Hruska has made a great effort in Rome to expand the applications of titanium to clinical dentistry (Hruska, 1990; Hruska and Borelli, 1991). He made recommendations for titanium casting, laboratory soldering, and intraoral welding of titanium for dental restorations. His most notable contribution (Hruska, 1987, 1989) was the welding of titanium in the mouth without harming adjacent living tissue, which could possibly yield a large

cost savings for dentists, patients, and insurance carriers, since this method solves certain problems in the area of clinical fixed prosthodontics.

Porcelain veneering

With the present demands for esthetic restorations, a titanium restoration without porcelain veneering would not be well accepted. Compared to veneering porcelain on a conventional dental alloy, there are two major problems in attaining an acceptable bond between titanium and a dental ceramic: (1) the high reactivity of titanium with oxygen, especially at temperatures greater than 800°C (Togaya *et al.*, 1983), and (2) the low linear coefficient of thermal expansion of titanium compared to the conventional porcelain-fused-to-metal (PFM) alloys ($9.4 \times 10^{-6}/^{\circ}\text{C}$ versus $13\text{-}16 \times 10^{-6}/^{\circ}\text{C}$) (Togaya *et al.*, 1983). Since the peak firing temperature of currently available dental porcelains for veneering is approximately 1000°C and their coefficient of thermal expansion ranges from $12\text{-}14 \times 10^{-6}/^{\circ}\text{C}$ (Craig, 1993, p. 492), it is necessary to develop a new ceramic system specifically for this purpose. During the last 10 years, several attempts to overcome the problems listed above have been made by various investigators. As early as 1983, Togaya *et al.* (1983) published experimental data which indicated that a bond strength on the order of 77 MPa between unalloyed titanium (not cast titanium but a commercial ingot) and experimental porcelains with a low coefficient of thermal expansion ($8.5\text{-}8.9 \times 10^{-6}/^{\circ}\text{C}$) could be attained using a low firing temperature near 750°C. More recent findings (Hautaniemi and Herø, 1991; Derand and Herø, 1992; Hautaniemi *et al.*, 1992, 1993) suggest that: (1) sometimes the reaction-affected, brittle, hardened surface layer of the cast titanium needs to be removed (50-100 μm) in order to make the layer of titanium oxide adhere to the titanium and substrate; (2) an important factor in improving bonding is surface roughness (mechanical interlocking); and (3) a thin oxide layer on the titanium formed during firing produces a system with better bonding and thus, firing under a better level of vacuum produces stronger bonding between the porcelain and the titanium. Hautaniemi and Herø (1991), similar to Togaya *et al.* (1983), used a porcelain with a low linear thermal expansion coefficient (by eliminating the leucite crystals) in testing the bond strength, and reported that a minimal thermal expansion mismatch and better bonding between the titanium and porcelain was obtained. Thus far, more than five different porcelain systems for veneering on titanium are on the market, and studies examining these products are being initiated [the review by Meyer (1993) gives some examples].

Dental Applications of Titanium Using Methods Other Than Casting

Superplastic forming

Superplasticity is the ability of a material to with-

stand very large deformations in tension without forming a neck (Dieter, 1986). This phenomenon was discovered as early as 1920, but more attention has been given to it since the 1960's after complex metal shapes were found to be readily formed under superplastic conditions. Superplastic behavior occurs at $T > 0.5 T_f$ (T_f = fusion temperature) for some metals having a grain size or interphase spacing on the order of 1 μm during deformation at a low strain rate. High strain rate sensitivity (> 0.4) is another characteristic of superplastic metals and alloys. One of the industrial titanium alloys being considered for dental use, Ti-6Al-4V, has this unique property (Okuno *et al.*, 1989). Presently, one Japanese company has begun to sell a unit for producing full denture bases using this technique. When heated at 850-900°C, the $\alpha + \beta$ two-phase Ti-6Al-4V alloy with a grain size of several micrometers exhibits elongation of more than 1000% at a strain rate near 0.5%/sec (Okuno, 1988c). The fabrication of bases for entire maxillary prostheses was attempted in Japan using this alloy. During actual production, as explained by Meyer (1993), a fine-grained Ti-6Al-4V alloy sheet approximately 0.5 mm thick is placed on a model prepared with phosphate-bonded investment that is strengthened by heating prior to the operation. This is placed in a vacuum enclosure, then protected by a flow of argon. The temperature is increased gradually to 950°C over 30 minutes to 1 hour at a pressure of 7-8 kg/cm². A denture base made with this technique is reported to have an acceptable adaptability to the model to within a tolerance of less than 0.1 mm (Ito *et al.*, 1989). The degree of fit to the model was reported to be even better than that obtained from a conventional Co-Cr casting. In addition, the surface of the Ti-6Al-4V denture base made by superplastic forming is shown to be much smoother than that of a Co-Cr alloy casting made by a traditional method.

At least two other experimental methods using metal deformation processes have been investigated in order to produce dental appliances. These are cold electromagnetic deformation and impulsive hydraulic pressure forming (Meyer, 1993). In the former method, magnetic pressure is generated, and the stored energy is released within a short period of time to form crowns. The latter method utilizes a similar procedure with hydraulic pressure created through a liquid transmitter to produce entire maxillary prostheses. It is claimed that appliances made with these techniques are accurate enough for clinical applications.

Electrical discharge machining and milling

Electrical discharge machining and/or milling of blocks of titanium ingot have been examined by some investigators as an alternative method to casting to make crowns. One of the advantages of this method of making crowns is better fit of the restorations to the prepared teeth compared to that of cast titanium crowns.

The method developed by Swedish researchers (Andersson *et al.*, 1989) involves machine duplication of the outer surfaces of the crown and electrical discharge machining of the interior from unalloyed titanium ingots. They have already performed clinical trials of these titanium crowns after veneering the surface with either composite materials (Isosit, Ivoclar, Liechtenstein, and Dentacolor, Kulzer, Germany) (Bergman *et al.*, 1990, 1994) or a ceramic (Porcera ceramic, Ducera, Rosbach, Germany) (Nilson *et al.*, 1994). In either case, acceptable clinical performance was found; the failure rate of the composite (Dentacolor)-veneered crowns between 51 and 72 months was reported to be 9.4% after examining 85 units. The failure rate from fracture of the porcelain-veneered crowns was 2 out of 44 units examined between 26 and 30 months (Nilson *et al.*, 1994). They reported that the marginal integrity of all the porcelain-veneered crowns was satisfactory, and the majority were rated excellent. In a recent article, Miyazaki (1992) reported that two other methods being examined include: (1) a (DCS) titanium system in which titanium copings are made by milling on both the inside and the outside from a titanium ingot using data obtained from a needle-densitizer on a stone model; and (2) a combined method of wire-electrical discharge machining and milling with information received from measurements using a laser beam. No clinical trials of these crowns have been reported.

It should be added that, unlike the casting process, the electrical discharge machining method of fabricating crowns and inlays has not yet been commercialized. Therefore, the success of this method largely depends on how rapidly an economical process comparable to the casting technique can be developed.

Metal forming

Because of the extensive development of the titanium industry over the past 40 years, ingots of unalloyed titanium can be rolled into plates and rods using mill facilities similar to those used for steel and other non-ferrous alloys. Although the processing of titanium alloys requires more complicated procedures, titanium alloy plates and wires can be fabricated as readily as wrought unalloyed titanium products.

Orthodontic applications. Some titanium alloys (β -titanium) have been evaluated for use as orthodontic appliances since these alloys exhibit relatively low moduli of elasticity and high yield strengths which allow them to impart low force per unit activation and to sustain large deflections without permanent deformation (Burstone and Goldberg, 1980). In addition, these alloys have excellent formability (β phase) and can be welded. Several multi-component alloys, including Ti-15V-3Cr-3Al-3Sn, have been examined *in vitro* and are reported to have improved formability and spring-back in clinical usage (Wilson and Goldberg, 1987). A nickel-titanium alloy (NiTi or nitinol) wire has also been

introduced for clinical use (Andreassen and Morrow, 1978; Sachdeva and Miyazaki, 1990). Unlike other traditional orthodontic wires, some NiTi wires exhibit unique mechanical properties called "superelasticity" or more exactly, "pseudoelasticity", and also "shape memory" effect.

Pseudoelasticity is the result of stress-induced martensitic transformation which returns the metal to its parent phase upon unloading (Meyers and Chaula, 1984). Stressing an alloy having this capability at a temperature higher than the M_s temperature initially results in stress-strain behavior which is seen in the deformation of a common metal within the proportional limit. During phase transformation, there is an appreciable increase in strain due to the volume change resulting from the change in the crystal structure: the structure for the austenite phase is ordered bcc (CsCl-type), and the martensitic structure has been described as based upon a distorted monoclinic, triclinic or hexagonal unit cell (Wang *et al.*, 1972; Miura *et al.*, 1986; Goldstein *et al.*, 1987). Upon unloading, the martensite reverts to the parent phase, and further unloading results in the return of the alloy to the original length (or shape). This characteristic is desirable in some orthodontic situations because the wire delivers a relatively constant force for a large displacement and thus has a very large working range or springback (Phillips, 1991, pp. 456-457) when the material undergoes this phenomenon. Many products with variations in the alloy phase(s), degree of cold work, and transition temperature are available. A further advantage of this type of wire for orthodontic application is that heat treatment enables the load magnitude at which superelasticity is exhibited to be influenced and controlled by both temperature and time. Unfortunately, one of the drawbacks of NiTi wires is that they are difficult to form and they must be joined mechanically since the alloy can neither be soldered nor welded (Phillips, 1991, p. 457). Even though the biocompatibility of the NiTi alloy has been well documented, some other superplastic titanium alloys, which do not contain nickel, have been developed for patients with nickel sensitivity. Recently, TiPd and TiPd+Cr alloys were evaluated for use in orthodontic wires and denture clasps in addition to their application to dental and medical implants (Enami *et al.*, 1989).

Besides having the pseudoplastic property mentioned above, NiTi type alloys also have the shape-memory effect. This is the phenomenon by which, after being deformed at one temperature, the alloy returns to the original shape upon being heated to a second temperature (Meyers and Chaula, 1984). This is because the austenite to martensite transformation occurs by a reversible twinning process. The recent introduction of body temperature-activated, shape-memory NiTi wires exploits these principles, but clinical studies to verify the improved efficacy of these products have not been performed. Brantley (1989) has written a brief summary on

the metallurgical and clinical aspects of β -titanium orthodontic wires as well as nickel-titanium orthodontic alloys.

Applications to maxillofacial implantology Because of their excellent biocompatibility, various applications of titanium and its alloys to maxillofacial surgery have been made over the last 20 years. Generally, in this area, wrought prefabricated pieces are used for various mandibular reconstructions. With improvements in surgical implantation techniques, implant designs, and surface finishes, these titanium fixtures have shown considerable clinical success (Lautenschlager and Monaghan, 1993). As a matter of fact, Szurgot *et al.* (1988) cast complex patterns of pure titanium using the Ohara equipment and indicated a possible application of titanium to both medicine and dentistry.

Summary

In this paper, recent information on the technology related to the use of titanium in a major area of dentistry has been reviewed. Initial research investigating the feasibility of casting titanium for dental prostheses that began a little more than 15 years ago by pioneering research teams in two countries, one led by Waterstrat at NIST in the U.S. and one directed by Ida of Kyoto University, has now created a great deal of interest not only among academic researchers but also in numerous industries worldwide. Those who contributed to the development of today's dental applications of titanium deserve a lot of credit. It now appears that some of the major problems related to titanium casting have been solved and that titanium can seriously be considered as an addition to the list of existing dental casting metals and alloys. However, a number of problems still have to be overcome before dental titanium technology will be accepted as an economical way to cast various prosthetic appliances. Further development is needed to obtain more efficient casting equipment, a less reactive investment material with the desired expansion capability, and a specifically designed ceramic system.

Other fabrication methods for dental appliances which do not use casting such as superplastic forming, the combination of electrical discharge machining and milling, and powder metallurgical methods will continue to compete as other ways to produce titanium crowns, bridges, and dentures.

More than anything else, the strength of titanium as a dental material lies in its proven biocompatibility compared to many other dental materials presently used and also in its abundance (the ninth most abundant element on earth). In the foreseeable future, it will be very surprising if this metal is not developed and routinely used in the field of dental prosthetics.

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A tremendous number of abstracts, papers, and other documents on the application of titanium to dentistry have been published throughout the world. Unfortunately, many important studies had to be left out of the present review. It was not the intent of the authors to ignore these studies; however, it was impossible to include all of them in this paper.

References

- Andersson M, Bergman B, Bessing C, Ericson G, Lundquist P, Nilson H (1989). Clinical results with titanium crowns fabricated with machine duplication and spark erosion. *Acta Odontol Scand* **47**: 279-286.
- Andreassen GF, Morrow RE (1978) Laboratory and clinical analysis of nitinol wire. *Am J Orthod* **73**: 142-151.
- ASM (1985). *Metals Handbook*, Desk Edition. American Society of Metals, Metals Park, Ohio. p. 1.52.
- Beder OE, Ploger WJ (1959). Intraoral titanium implants. *Oral Surg, Oral Med, Oral Path* **12**: 787-799.
- Bergman B, Bessing C, Ericson G, Lundquist P, Nilson H, Andersson M (1990). A 2-year follow-up study of titanium crowns. *Acta Odontol Scand* **48**: 113-117.
- Bergman B, Nilson H, Andersson M (1994). Denta-color® as veneering material for titanium. *Swed Dent J* **18**: 25-28.
- Bothe RT, Beaton LE, Davenport HA (1940). Reaction of bone to multiple metallic implants. *Surg Gynecol Obstet* **71**: 598-602.
- Boyer R, Welsch G, Collings EW (1994). *Materials Properties Handbook: Titanium Alloys*. ASM International, Materials Park, OH. p. 178, 1079.
- Brantley WA (1989). Orthodontic wires. In: *Dental Materials: Properties and Selection*. O'Brien WJ (ed.). Quintessence Publishing Co., Lombard, IL. pp. 381-395.
- Brodersen C, Prasad A (1992). System and method for casting and reworking metallic material. United States patent 5,161,600.

- Burstone CJ, Goldberg AJ (1980). Beta titanium: A new orthodontic alloy. *Am J Ortho* **77**: 121-132.
- Clarke EGC, Hickman J (1953). An investigation into the correlation between the electric potential of metals and their behaviour in biological fluids. *J Bone Joint Surg Br* **35B**: 467-473.
- Collings EW (1988). Introduction to titanium alloy design. In: *Alloying*. Water JL, Jackson MR, Sims CT (eds.). ASM Internatl., Metals Park, OH. pp. 257-370.
- Craig RG (1993). *Restorative Dental Materials*. 9th ed. C.V. Mosby Co., St. Louis. p. 395, 426, 492.
- Derand T, Herø H (1992). Bond strength of porcelain on cast vs. wrought titanium. *Scand J Dent Res* **100**: 184-188.
- Dieter GE (1986). *Mechanical Metallurgy*. 3rd ed. McGraw-Hill Book Co., New York. p. 452
- Donachie MJ (ed.) (1988). *Titanium: A Technical Guide*. ASM Internatl., Metals Park, OH. p. 14, 28, 69, 71, 133, 159, 162, and 353.
- Enami K, Horii K, Takahashi J (1989). Martensitic transformation in TiPd-Cu alloys. *ISIJ (Iron and Steel Institute of Japan) International* **29**: 430-437.
- Flemings MC (1974). *Solidification Processing*. McGraw-Hill Book Co., New York. pp. 219-224.
- Goldstein D, Kabacoff L, Tydings J (1987). Stress effects on nitinol phase transformations. *J Metals* **39**: 19-26.
- Greener EH (1990). Titanium casting in the U.S.A. Presented at the First International Symposium on Titanium in Dentistry, Frankfurt, Germany (copy available from T. Okabe, address at page 211).
- Greener EH, Moser JB, Opp J, Szurgot K, Marker BC (1986). Properties of centrifugally cast commercial Ti and Ti-6Al-4V. *J Dent Res* **65**: 317 (abstract 1329).
- Hamanaka H (1993). Titanium casting - A review of casting machines. In: *Transactions, Second International Congress on Dental Materials*. pp. 89-96 (available from K. Anusavice, Univ. Florida Col. Dentistry, Gainesville).
- Hanawa T, Ota M (1992). Reactivity of metallic biomaterials with ions and molecules existing in biological systems. *J Jpn Soc Metals* **31**: 422-428 (in Japanese).
- Hashimoto H, Kuroiwa A, Wada K, Hibino Y, Kouchi H, Hashimoto T, Hasegawa Y, Ando Y, Akaiwa Y (1992). Reaction products on the surface of titanium castings. *J Jpn Soc Dent Mater Dev* **11**: 603-614.
- Hautaniemi JA, Herø H (1991). Effect of crystalline leucite on porcelain bonding on titanium. *J Amer Ceram Soc* **76**: 1449-51.
- Hautaniemi JA, Herø H, Juhanoja JT (1992). On the bonding of porcelain on titanium. *J Mater Sci* **3**: 186-191.
- Hautaniemi JA, Juhanoja JT, Herø H (1993). Porcelain bonding on Ti: Its dependence on surface roughness, firing time, and vacuum level. *Surf Interface Anal* **20**: 421-426.
- Herø H, Syverud M, Waarli M, Jørgen RB (1990). Casting of dental Ti crowns: Surface reactions and dimensional fit. In: *Proceedings of the 1990 International Conference on Titanium Products and Applications, Vol. II*. Titanium Development Association. pp. 612-621 (copy available from H. Herø, address at page 211).
- Herø H, Syverud M, Waarli M (1993a). Mold filling and porosity in castings. *Dent Mater* **9**: 15-18.
- Herø H, Syverud M, Waarli M (1993b). Porosity and mould filling of titanium castings. *J Mater Sci* **4**: 296-299.
- Hruska AR (1987). Intraoral welding of pure titanium. *Quintessence International* **18**: 683-688.
- Hruska AR (1989). Welding implants in the mouth. *J Oral Implant* **15**: 198-203.
- Hruska AR (1990). A novel method for vacuum casting titanium. *Int J Prosthodont* **3**: 142-145.
- Hruska AR, Borelli P (1991). Quality criteria for pure titanium casting, laboratory soldering, intraoral welding, and a device to aid in making uncontaminated castings. *J Prosthet Dent* **66**: 561-565.
- Ida K (1986). Dental casting technique for titanium: The present status in Japan. *Transactions, The Academy of Dental Materials Symposium on Dental Applications of Titanium and Its Alloys* (available from K. Anusavice, Univ. Florida Col. Dentistry, Gainesville).
- Ida K (1991). Titanium casting in dentistry: Present status in Japan. In: *Titanium: From Mining to Biomaterials. Proceedings of the Wollongong Symposium*. Jones AJ (ed.). Department of Industry, Technology and Commerce, Canberra, Australia. pp. 63-71.
- Ida K, Togaya T, Suzuki M (1983). Mechanical properties of cast pure titanium and its alloys: An evaluation as candidates for dental casting alloys. *J Jpn Soc Dent Mater Dev* **2**: 765-771.
- Ito M, Okuno O, Ai M, Miura I (1989). Application of superplastic titanium alloy for denture base. Part I: Adaptability of the titanium alloy denture base. *Kokubyo Gakkai Zasshi* **56**: 429-434 (in Japanese).
- Kawazoe T (1992). Clinical applications of fixed prosthodontic restorations made of pure titanium. In: *Proceedings, 5th Meeting of the Society for Titanium Alloys in Dentistry and 2nd International Symposium on Titanium in Dentistry* (in Japanese; available from Inst. Med. and Dental Engg., Tokyo Medical and Dental Univ., Chiyoda-ku, Tokyo, Japan).
- Kubaschewski O, Alcock CB (1979). *Metallurgical Thermochemistry*. 5th ed. Pergamon Press, Oxford. pp. 268-284.
- Lautenschlager EP, Monaghan P (1993). Titanium and titanium alloys as dental materials. *Int Dent J* **43**: 245-253.
- Lechner SK (1991). Osseointegrated titanium implants in prosthodontics. In: *Titanium: From Mining to Biomaterials. Proceedings of the Wollongong Symposium*. Jones AJ (ed.). *op. cit.* pp. 55-61.

- Leventhal GS (1951). Titanium, a metal for surgery. *Joint Surgery* **33A**: 473-474.
- Meyer JM (1993). Le titane en dentisterie: Quels développements jusqu'à ce jour? (Titanium in Dentistry: What are the Developments Up to the Present?). *J Biomat Dent* **8**: 5-30 (in French).
- Meyers MA, Chaula KK (1984). *Mechanical Metallurgy: Principles and Applications*, Prentice Hall, Inc., Englewood Cliffs, NJ. pp. 487-490.
- Miura F, Mogo M, Ohura Y, Hamanaka H (1986). The super-elastic property of the Japanese NiTi alloy wire for use in orthodontics. *Am J Orthod Dentofac Orthop* **90**: 1-10.
- Miyakawa O, Watanabe K, Okawa S, Nakano S, Kobayashi M, Shiokawa H (1989). Layered structure of cast titanium surface. *Dent Mat J* **8**: 175-185.
- Miyakawa O, Wanabe K, Okawa S, Nakano S, Shiokawa H, Kobayashi M, Tamura H (1991). Near surface structure and mechanical properties of titanium cast in various atmospheres. *J Jpn Soc Dent Mater Dev* **10** (Spec. Issue 7): 18-19.
- Miyazaki T (1990). Current research and development of casting apparatus for titanium. *Quintessence of Dental Technology* **15**: 122-126 (in Japanese).
- Miyazaki T (1992). Recent progress in titanium dental casting technology and current problems for clinical applications. *The Quintessence (Tokyo)* **11**: 171-182 (in Japanese).
- Miyazaki T (1993). Recent advances in investment materials for titanium castings. In: *Transactions, Second International Congress on Dental Materials* (available from K. Anusavice, Univ. Florida Col. Dentistry, Gainesville). pp. 107-116.
- Mueller HJ, Reyes WD, Moser JB, Giuseppetti A, Waterstrat RM (1988). Particle-, pore-size distribution and thermal behavior of investments for titanium. *J Dent Res* **67**: 345 (abstract 1861).
- Mueller HJ, Giuseppetti AA, Waterstrat RM (1990). Phosphate-bonded investment materials for titanium casting. *J Dent Res* **69**: 367 (abstract 2072).
- Murray JL (ed.) (1987). *Phase Diagram of Binary Titanium Alloys*. ASM International, Metals Park, OH. p. 1.
- Nakamura H (1988). Investment materials for casting titanium. In: *Applications of Titanium in Dentistry*. Miura I, Ida K (eds.). Quintessence Books, Tokyo. pp. 62-72 (in Japanese).
- Nilson H, Bergman B, Bessing C, Lundquist P, Andersson M (1994). Titanium copings veneered with Procera ceramics: A longitudinal clinical study. *Int J Prosth* **7**: 115-119.
- O'Brien WJ (1989). *Dental Materials: Properties and Selection*. Quintessence Publishing Co., Lombard, IL. p. 550.
- Okuda R (1993). Present status of dental titanium casting. *Dental Diamond* **18**: 29-43 (in Japanese).
- Okuno O (1988a). Titanium alloys for casting. In: *Application of Titanium in Dentistry*. Miura I, Ida K (eds.). Quintessence Books, Tokyo. pp. 51-61 (in Japanese).
- Okuno O (1988b). Prosthodontic applications of titanium. *Shika Dent J* **27**: 531-539 (in Japanese).
- Okuno O (1988c). An application of titanium's superplasticity to dentistry. *Dent Eng* **85**: 28-31 (in Japanese).
- Okuno O (1991). Issues on titanium casting. *Shika Giko* **19**: 79-85 (in Japanese).
- Okuno O, Hamanaka H (1989). Application of beta titanium alloys in dentistry. *Dentistry in Japan* **26**: 101-104.
- Okuno O, Shimizu A, Miura I (1985). Fundamental study on titanium alloys for dental casting. *J Jpn Soc Dent Mat Dev* **4**: 708-715.
- Okuno O, Nakano T, Miura I (1987). Introducing routine lab works of titanium by using alloyed titanium. *Shika Giko* **15**: 1015-1023 (in Japanese).
- Okuno O, Nakano T, Hamanaka H, Miura I, Ito M, Ai M, Okada M (1989). Superplastic forming of titanium alloy denture base. *J Jpn Dent Mat Dev* **8**: 129-136 (in Japanese).
- Phillips RW (1991). *Skinner's Science of Dental Materials*. 9th ed. W.B. Saunders Co., Philadelphia. pp. 456-457.
- Prasad A, Broderson C, Day, GP, Garcia F, Weissbecker H, Kobakov Y (1994). Dense titanium castings: The promise fulfilled. *Trends Tech Contemp Dent Lab* **10**: 94-97.
- Pröbster L, Geis-Gerstorfer J, Simonis A, Setz J, Weber H (1991). Titan - zum gegenwärtigen Stand eines neuen Dentalwerkstoffes (Titan - A New Dental Material). *dental-labor* **39**: 1073-1078 (in German).
- Rappo JO (1994). Cast titanium frameworks for fixed prostheses: Castability, marginal adaptation, and ceramic bond strength. In: *Abstracts, First Information Meeting on Titanium in Dentistry in Switzerland*. Meyer JM, Belser U (eds). pp. 97-102 (copy available from T. Okabe, address at page 211).
- Rupp NW, Waterstrat RM, Giuseppetti AA, Conner ML (1987). Cast titanium restorations: Clinical observations. *J Dent Res* **66**: 247 (abstract 1121).
- Sachdeva RCL, Miyazaki S (1990). Superelastic Ni-Ti alloys in orthodontics. In: *Engineering Aspects of Shape Memory Alloys*. Duerig TW, Melton KN, Stockel D, Wayman CM (eds.). Butterworth-Heinemann, London. pp. 452-469.
- Stoll R, Okuno O, Ai M, Stachniss V (1991). The technology of titanium casting: Possibilities, problems and expectations. *ZWR (Zahnärztliche Welt, Zahnärztliche Rundschau)* **100**: 38-42 (in German).
- Sunnerkrantz PA, Syverud M, Herø H (1990). Effect of casting atmosphere on the quality of Ti-crowns. *Scand J Dent Res* **98**: 268-72.
- Szurgot KC, Marker BC, Moser JB, Greener EH (1988). The casting of titanium for removable partial

dentures. Renner RP (ed.). QDT Yearbook. Quintessence Publishing Co., Lombard, IL. pp. 171-176.

Taira M, Moser JB, Greener EH (1989). Studies of Ti alloys for dental castings. *Dent Mater* 5: 45-50.

Takahashi J, Kimura H, Lautenschlager EP, Chern Lin JH, Moser JB, Greener EH (1990). Casting pure titanium into commercial phosphate-bonded SiO₂ investment molds. *J Dent Res* 69: 1800-1805.

Takanashi T (1993). Tycast system. In: *The Dental Technology of Titanium. Quintessence of Dental Technology, extra issue.* Quintessence Pub. Co., Tokyo. pp. 137-143 (in Japanese).

Takeuchi M, Togaya T, Tsutsumi S, Ida K (1978). A new dental casting machine utilizing argon arc melting and argon gas flow casting. *J Jpn Soc Dent Mater Dev* 35: 245-250.

Tanaka N (1993). A titanium casting system. *J Nihon Univ. School of Dental Technicians* 11: 33-40 (in Japanese).

Tani Y (1991). The use of titanium in dentistry. In: *Titanium: From Mining to Biomaterials. Proceedings of the Wollongong Symposium.* Jones AJ (ed.). *op. cit.* pp. 47-54.

Togaya T (1986). A study of pure titanium and its alloys for application in dental use. *Gifu Shigaku-kai Shi* 13: 60-93 (in Japanese).

Togaya T (1990). A new titanium casting machine. *Shika Giko* 18: 1394-1402 (in Japanese).

Togaya T (1993). Selecting investment materials for better casting accuracy. *Shika Giko* 21: 910-917 (in Japanese).

Togaya T, Tani Y (1989). Titanium casting techniques. *Shika Journal* 30: 379-388 (in Japanese).

Togaya T, Yabugami M, Ida K (1981). Studies on the dental casting of titanium alloy: Part IV. Casting of pure titanium alloys with magnesia investment. *J Jpn Soc Dent Mater Dev* 38: 460-467.

Togaya T, Suzuki M, Tsutsumi S, Ida K (1983). An application of pure titanium to the metal porcelain system. *Dent Mater J* 2: 210-219.

Togaya T, Suzuki M, Ida K, Nakamura M, Uemura T, Okuda S (1985). Studies on magnesia investment for casting of titanium: Improvement of fitness on castings by utilizing an expansion due to oxidation of additive Zr powder in the investment. *J Jpn Soc Dent Mater Dev* 4: 344-349.

Vitik AJ (1991). Titanium dental castings, cold-worked titanium restorations - Yes or no? *Trends Tech Contemp Dent Lab* 7: 23-34.

Wang FE, Pickert SJ, Alperin HA (1972). Mechanism of the TiNi martensitic transformation and the crystal structures of TiNi-II and TiNi-III phases. *J Appl Phys* 43: 97-112.

Waterstrat RM (1977). Comments on casting of Ti-13Cu-4.5Ni alloy. Publication No. (NIH) 77-1227. US Dept. Health, Education and Welfare, Washington DC. pp. 224-233.

Waterstrat RM (1987). State of the art in titanium casting. *Trends Tech Contemp Dent Lab* 4: 46.

Waterstrat RM, Giuseppetti AA (1985). Casting apparatus and investment mold material for metals which melt at very high temperatures. *J Dent Res* 64: 317 (abstract 1278).

Waterstrat RM, Rupp NW, Franklin O (1978). Production of a cast titanium-base partial denture. *J Dent Res* 57: 254 (abstract 717).

Williams DF (1981). *Systemic Aspects of Biocompatibility, Vol. I.* CRC Press, Boca Raton, Florida. pp. 170-177.

Wilson DF, Goldberg AJ (1987). Alternative beta-titanium alloys for orthodontic wires. *Dent Mater* 3: 337-341.

Yoneyama T, Doi H, Hara M, Hamanaka H (1990). Influence on mechanical properties of pure titanium casting. Part I: Titanium ingots and vacuum degree in the melting chamber. *Tokyo Medical and Dental University Rep Inst Med Dent Eng* 24: 5-10 (in Japanese).

Zhang J, Okazaki M, Takahashi J (1994). Effect of casting methods on surface state of pure titanium castings. *J Jpn Soc Dent Mater Dev* 13: 221-227.

Discussion with Reviewers

Reviewer I: You state in the text: "When an investment with a high enough permeability was used, the mold was completely filled. These results indicate that the adjustment of the mold permeability was crucial to obtaining a sound, complete casting." It is all right in research to have multiple sample of the same geometry (such as the 5-unit bridge in Herø's work) to find the optimum gas pressure and the resulting soundness of the casting. This luxury is, however, not afforded to the laboratory. The work of Herø *et al.* does provide valuable information that too high a pressure difference is counter-productive.

Authors: The authors believe that the incomplete mold filling in the referred experiments is basically due to the permeability of the mold. The pressure difference most likely has no influence on the mold filling. The question of adjusting the Ar pressure in commercial casting equipment is not our problem. However, we are sure that it can easily be achieved by the manufacturers of the casting machines if they wish to do so.

R.M. Waterstrat: Cast dental appliances that contain internal voids can often give acceptable service even when the voids are relatively large. The extent to which such voids exist in clinical practice is not easily determined unless the casting is inspected by X-rays and most of them are not. If they are inspected, it is usually the dentist who performs the inspection using a dental X-ray machine. These X-ray machines are generally incapable of sufficient penetration to reveal internal voids in relatively thick castings of high density such as gold alloys or nickel-base alloys. These X-ray machines are capable

of penetrating most titanium castings, however, because of titanium's lower density. Thus, one easily sees voids in titanium castings that would be impossible to see in gold or nickel-based castings. One can gain a false impression, therefore, that titanium castings contain more voids or larger voids than those that are present in other dental alloys when in fact, there may be no significant difference. When this masking effect by higher-density alloys is taken into consideration, is there any significant difference in void content between properly prepared titanium castings and castings of other alloys?

Authors: It is true that it is difficult to detect porosity in noble metal and Ni-Cr alloys by X-ray radiography. Nevertheless, because of the high reactivity and the large difference between the melting point and the mold temperature for titanium, the tendency to porosity in titanium castings is most likely higher than for conventional dental casting alloys. Large titanium castings, in particular, suffer from the porosity problem (Donachie, 1988, p. 106). On the other hand, by using adequate and special equipment for casting of titanium dental appliances, the porosity problem can, be largely overcome.

R.M. Waterstrat: Can the authors give an estimate of the cost of preparing a titanium crown or partial denture as compared with an equivalent appliance cast from a dental nickel-chromium alloy, for example? How significant would the capital investment be to enable an ordinary dental laboratory to acquire the ability to produce titanium castings?

Authors: The cost of a casting machine for titanium is generally higher than those for conventional alloys and will often be on the order of \$35,000. This will, to some extent, reduce the benefits of the lower price for titanium compared with gold. Otherwise, we do not have information about the costs of producing dentures of titanium compared with noble metal and Ni-Cr alloys.

R.M. Waterstrat: How does one evaluate the so-called "alpha-case" on castings of pure titanium that are composed entirely of the alpha-phase?

Authors: "Alpha-case" is the solid solution-hardened surface zoned due to inward diffusion of contaminating elements like oxygen and nitrogen (Donachie, 1988, p. 28). These elements tend to stabilize the α -phase in titanium. The hardness decreases gradually with distance from the surface. The extent of this surface zone in crowns and bridges of cast titanium has often been observed to be in the range of 50-100 μm , depending on several factors: the thickness of the casting, atmosphere, mold temperature, investment composition, etc.

R.M. Waterstrat: Can the authors provide any information on patients' opinions regarding the acceptability of titanium appliances?

Authors: We are not aware of any publications related to patients comments about titanium crowns and bridges.

W.A. Brantley: The authors note the importance of very low impurity concentrations in determining the mechanical properties of the four ASTM grades of unalloyed [commercially pure (CP)] titanium. Could the authors briefly describe the analytical procedures used by the manufacturers to determine these impurity concentrations and provide some general comments on the accuracy of the values obtained?

Authors: The methods applied for analyses of the impurities in question are often based on gas chromatography. It is difficult to give a general level of accuracy for these methods.

W.A. Brantley: Taira *et al.* (1989) describe the coarse-grained microstructures which occurred in their titanium alloy castings and pointed out the need for a suitable grain-refining element for cast titanium alloys analogous to iridium and ruthenium which have been successfully employed for the gold-based and palladium-based dental casting alloys? Are grain-refining elements now available for titanium dental casting alloys?

Authors: We do not know about papers on grain size control or grain refining elements for titanium castings.

W.A. Brantley: The authors note that Okuno *et al.* (1985) and Okuno and Hamanaka (1989) have considered a variety of β titanium alloys and have suggested that Ti-20Cr-0.2Si and Ti-25Pd-5Cr appear well-suited for prosthodontic applications. Do these alloys have single-phase microstructures? What is the status of research on the *in vitro* corrosion behavior of these alloys? There might be concern about electrochemically active secondary phases or significant reduction in the passive behavior of these interesting new titanium alloys. Also, could the authors briefly comment on whether cytotoxicity or other biocompatibility studies have been performed on the new titanium casting alloys discussed in their article?

Authors: The phase diagrams for the two alloys mentioned show that they are clearly not single phased. As far as we know, no one has examined the biocompatibility or corrosion behavior of these alloys.

W.A. Brantley: Please elaborate on the DCS process.

Authors: It consists in a form recognition procedure based on sensing, by a manually driven device, the shape of a gypsum model of the prepared tooth. The three-dimensional (3D) data are recorded in a computer file. A computer program allows then the 3D design of the form of the crown to be produced, and the computation of the movements of the cutting tool in the multi-axis cutting machine. This program is then used by the machine to actually produce the crown from a solid block of pure or alloyed titanium. For bridges, the shapes of the abutment teeth are sensed, and the 3D designing program is used to create and incorporate the pontics to form the completed bridge.