Grindability of Dental Cast Ti-Ag and Ti-Cu Alloys

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Received January 14, 2003/Accepted March 28, 2003

Experimental Ti-Ag alloys (5, 10, and 20 mass% Ag) and Ti-Cu alloys (2, 5, and 10 mass% Cu) were cast into magnesia molds using a dental casting machine, and their grindability was investigated. At the lowest grinding speed (500 m·min⁻¹), there were no statistical differences among the grindability values of the titanium and titanium alloys. The grindability of the alloys increased as the grinding speed increased. At the highest grinding speed (1500 m·min⁻¹), the grindability of the 20% Ag, 5% Cu, and 10% Cu alloys was significantly higher than that of titanium. It was found that alloying with silver or copper improved the grindability of titanium, particularly at a high speed. It appeared that the decrease in elongation caused by the precipitation of small amounts of intermetallic compounds primarily contributed to the favorable grindability of the experimental alloys.

Key words: Titanium alloy, Grindability, Grinding

INTRODUCTION

Titanium is well suited for dental applications because of its combination of excellent biocompatibility and corrosion resistance, but it is difficult to process. Poor machinability (ease of cutting or grinding) is an obstacle to practical dental application of titanium, since cutting, grinding, and polishing of dental prostheses at dental laboratories or chair-side are essential. The poor machinability of titanium leads to a long processing time, poor surface finish, and short tool life. The same problems arise when milling titanium with recently developed dental CAD/CAM systems.

Many studies concerning the machinability of titanium and its alloys in dentistry were carried out. Experimental cutting or grinding tools have been developed to improve the grinding efficiency of titanium. Its poor machinability can be attributed mainly to its high melting temperature and high chemical reactivity at high temperatures, low thermal conductivity, and high ductility. Thus, titanium itself must be improved. One method of overcoming the present limitations of machinability is by alloying. However, most currently available dental alloys have been developed to facilitate the dental casting process. Because only a few have been developed for enhanced machinability, there is still room left for improvement.


Original paper

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Free-cutting titanium alloys were developed for industrial purposes\textsuperscript{(21)}. Taira et al. evaluated the machinability of the free-machining titanium using dental cutting instruments and found that it possessed better machining efficiency than titanium, which led to longer tool life\textsuperscript{(22)}. Watanabe et al. studied the machinability of cast free-cutting titanium alloy and compared it to that of titanium and Ti-6Al-4V\textsuperscript{(23)}. It was learned that the machinability of the free-cutting titanium was much better than that of titanium or Ti-6Al-4V when carbide burs were used. However, industrial free-cutting titanium alloy was developed without any consideration for dental use. Oda et al. evaluated the electrochemical behavior of a free-cutting titanium alloy and found that its corrosion resistance was inferior to that of pure titanium and that further consideration was needed before this alloy could be applied to dentistry\textsuperscript{(24)}.

In a previous study, experimental binary titanium alloys with 5, 10, and 20 mass\% Ag (hereafter, "mass\%" will be referred to as "\%") and 2, 5, and 10\% Cu were developed, and the mechanical properties and microstructures of their castings were examined\textsuperscript{(25)}. It was found that the Ti-Ag and Ti-Cu alloys, except for Ti-10\%Cu, possessed higher tensile and yield strength, and hardness than titanium, with sufficient ductility for dental prostheses. Furthermore, titanium alloyed with small amounts of silver or copper is reported to have acceptable corrosion resistance and biocompatibility for dental use\textsuperscript{(26–31)}. In the present study, the grindability of dental cast Ti-Ag and Ti-Cu alloys was evaluated, with the aim of developing a dental titanium alloy with better machinability than unalloyed titanium.

**MATERIALS AND METHODS**

**Composition of experimental alloys**

Both silver and copper are $\beta$-stabilizing elements, and Ti-Ag and Ti-Cu alloys are classified as titanium alloys with eutectoid transformation\textsuperscript{(32)}. The Ti-Ag alloy has a eutectoid point of $\alpha$-Ti and Ti$_2$Ag at 15.6\% Ag (7.6 mol\% Ag)\textsuperscript{(33)}. The Ti-Cu alloy has a eutectoid point of $\alpha$-Ti and Ti$_2$Cu at 7.0\% Cu (5.4 mol\% Cu)\textsuperscript{(34)}. In this study, experimental binary titanium alloys with 5, 10, and 20\% Ag (2.3, 4.7, and 10.0 mol\% Ag) and 2, 5, and 10\% Cu (1.5, 3.8, and 7.7 mol\% Cu) were examined. Ti-5\%Ag and 10\%Ag are located within the hypo-eutectoid region, and Ti-20\%Ag is located within the hyper-eutectoid region. Similarly, Ti-2\%Cu and 5\%Cu are located within the hypo-eutectoid region, and Ti-10\%Cu is located within the hyper-eutectoid region.

**Preparation of alloys**

Each alloy corresponding to a desired concentration was made by melting titanium sponge (>99.8\%, grade S-90, Sumitomo Sitix, Amagasaki, Japan) and silver (99.9\%, Hirano Seizaemon Shoten, Tokyo, Japan) or copper (99.99\%, The Research Institute for Electric and Magnetic Materials, Sendai, Japan) using an argon arc-melting furnace (TAM-4S, Tachibana Riko, Sendai, Japan) into buttons (15 g each). The chamber was evacuated to 5 mPa, and high-purity argon gas (>99.9999\%, Nipponsanso, Kawasaki, Japan) was introduced until the pressure reached 50 kPa prior to melting.
A titanium getter was melted before melting the material. Each ingot was inverted five times during melting and was melted six times in all. The titanium ingots were made in the same way.

**Preparation of specimens**
Wax patterns (3.5 mm×8.5 mm×30.5 mm) were invested in magnesia investment material (Selevest CB, Selec, Osaka, Japan). The molds were placed in a computerized furnace (KDF-009G, Denken, Kyoto, Japan) two hours after investing and were heated from room temperature to 850°C at a heating rate of 6°C·min⁻¹. After a one-hour holding period, they were cooled down to 200°C in the furnace. Each ingot was cast into the mold using an argon gas-pressure dental casting machine (CASTMATIC-S, Iwatani, Osaka, Japan). After casting, the molds were kept at room temperature. Prior to testing, 250 μm of the castings was removed from all the surfaces, producing specimens measuring 3.0 mm×8.0 mm×30 mm. Three specimens were made for each metal.

**Grindability test**
An experimental grindability tester equipped with an electric dental handpiece for dental laboratory use (MICROMOTOR LM-1, GC, Tokyo, Japan) was made based on the testing apparatus shown in JIS T5209 “Dental carborundum wheels”35. Carborundum (green silicon carbide) wheels [#4 (diameter 15.8 mm, thickness 1.6 mm); Shofu, Kyoto, Japan] were used as grinding tools. The diameter and weight of each wheel were measured before and after grinding. The thinner cross section (3.0 mm) of each specimen was ground at one of the five grinding speeds [500, 750, 1000, 1250, or 1500 m·min⁻¹ (8.3, 12.5, 16.7, 20.8, or 25 m·s⁻¹)] at 0.98 N (100 gf). The grinding speed was calculated from the diameter of the wheel and the free-running (unloaded) rotational speed of the handpiece. The grinding speed of 1500 m·min⁻¹ corresponded to about 3×10⁴ revolutions per minute, which was almost the maximum speed for the handpiece. In fact, the maximum revolutions per minute for regular use of the wheel is 3×10⁴, according to the manufacturer’s instruction. The specimen and the wheel were enclosed during grinding, and the metal chips were collected in a glass beaker.

The volume of metal removed during one minute of grinding was calculated from density previously measured using Archimedes’ principle and the weight loss of the specimen. Grindability was evaluated as volume of metal removed per minute (grinding rate) and volume ratio of metal removed compared to wheel material lost, which was calculated from its diameter loss (grinding ratio). The test was performed twice for each specimen and grinding speed. A new wheel was employed for every test. Results were compared among the titanium and the Ti-Ag or Ti-Cu alloys using one-way ANOVA followed by Scheffé’s test at α=0.05. The ground surfaces of the metals, metal chips, and surfaces of the wheels were examined using an electron probe microanalyzer (EPMA) with a wavelength-dispersive X-ray spectrometer (WDS) (JXA-8900R, JEOL, Tokyo, Japan).
Young's modulus

In addition to the tensile and Vickers hardness tests performed in a previous study, Young's modulus of each specimen was measured as a mechanical property using an ultrasonic pulser/receiver (Model 5800, Panametrics, Waltham, MA) and transducers (V208 and V156, Panametrics). Results were compared among the titanium and the Ti-Ag or Ti-Cu alloys using one-way ANOVA followed by Scheffé's test at α = 0.05. The strength of relationship between Young's modulus and the grindability was examined by analysis of correlation.

RESULTS

Grinding rate

The grinding rates of the Ti-Ag alloys are shown in Fig. 1 (a). At 500 m·min⁻¹, the rates of the Ti-Ag alloys were about the same as that of the titanium. There was no statistical difference in the grinding rate among Ti-5%Ag, Ti-10%Ag, and titanium at any speed. At 750 m·min⁻¹ or above, the grinding rate for Ti-20%Ag increased more than the speed ratio and was significantly higher than for the titanium. Appreciable sparking accompanied the grinding as the rotational speed increased, especially for the Ti-20%Ag alloy at 1250 m·min⁻¹ and above.

Fig. 1 (b) shows the grinding rates of the Ti-Cu alloys. At 500 m·min⁻¹, the rates of the Ti-Cu alloys were about the same as that of the titanium. There was an increase in the grinding rate of the Ti-Cu alloys as the concentration of copper increased. The grinding rates of Ti-5%Cu and Ti-10%Cu were significantly higher than that of titanium at 750 m·min⁻¹ and above. Considerable sparking also occurred with these alloys as the rotational speed increased, especially for the Ti-5%Cu and Ti-10%Cu alloys.
Ti-10%Cu at 1000 m·min⁻¹ and above.

The grinding rates of all the alloys at the highest grinding speed of 1500 m·min⁻¹ are summarized in Fig. 2. The rates increased as the concentration of silver or copper increased. Ti-20%Ag, Ti-5%Cu, and Ti-10%Cu exhibited significantly higher grinding rates than the titanium. The grinding rate for the 10% Cu alloy at 1500 m·min⁻¹ was the highest and was about 2.9 times larger than that for titanium. The grinding rate for the 20% Ag alloy at 1500 m·min⁻¹ was about 2.5 times as large as that for the titanium.

Grinding ratio
Regardless of the metal or grinding speed, the weight variation of the carborundum wheel during one minute of grinding was about 1 mg or less out of 0.6 g. As for the dimensions, the diameter decreased very slightly and randomly. Therefore, the grinding ratios, which were calculated using the amount of metal ground and wheel material lost, varied widely.

The grinding ratios of the Ti-Ag alloys are shown in Fig. 3(a). The ratios of the titanium were from 1.3 to 1.6 for all the grinding speeds. The grinding ratios of Ti-20%Ag increased as the speed increased. The Ti-20%Ag at 1500 m·min⁻¹ exhibited a significantly higher grinding ratio than did the titanium. The grinding ratios of the Ti-Cu alloys are shown in Fig. 3(b). The grinding ratio of Ti-10%Cu increased as the grinding speed increased. The Ti-10%Cu at 750 m·min⁻¹ and above exhibited significantly higher grinding ratios than did the titanium.

Fig. 4 summarizes the grinding ratios of all the alloys at the highest grinding speed of 1500 m·min⁻¹. The ratios of the experimental alloys increased as the
concentration of silver or copper increased. For Ti-20% Ag, Ti-5% Cu, and Ti-10% Cu, the ratios were significantly higher than that of the titanium. The grinding ratio of Ti-10% Cu at 1500 m·min⁻¹ was about 6.3 times larger than that of the titanium and was the highest, while the ratio of Ti-20% Ag at 1500 m·min⁻¹ was about 4.4 times larger than that of the titanium.
Fig. 5 Ground surfaces of the experimental titanium alloys.

Observation of metal chips, ground surfaces, and wheels

Fig. 5 shows electron micrographs of the ground surfaces of the metals at 500 m·min⁻¹ and 1500 m·min⁻¹. Grinding marks were observed for all the metals and speeds. Grinding burn (discoloration of the surface caused by the heat of grinding) was observed to a greater or lesser degree with most of the specimens ground at 1500 m·min⁻¹. At 500 m·min⁻¹, there was no clear difference in the appearance of
Fig. 6 Metal chips resulting from grinding at 1500 m·min⁻¹.

Fig. 7 Wheel surfaces (Intact and used to grind at 1500 m·min⁻¹).

the ground surface among the titanium and the experimental alloys. Notable adhesion of metal was observed for titanium ground at 1500 m·min⁻¹. On the other hand, the differences in the appearance of the ground surfaces of Ti-20%Ag, Ti-5%Cu, and Ti-10%Cu between the low speed and the high speed were less pronounced compared to the appearance of the titanium.

Fig. 6 shows electron micrographs of the metal chips resulting from grinding the titanium, Ti-20%Ag, Ti-5%Cu and Ti-10%Cu at 1500 m·min⁻¹. It appears that the metal chips of Ti-20%Ag and Ti-10%Cu are finer than those of the titanium. Fig. 7 shows electron micrographs of an intact wheel and of wheels used to grind at 1500 m·min⁻¹. The wear of some abrasive particles embedded in the matrix of the wheel (dulling) or adhesion of metal on the wheel surface (loading) was found. Fine powdery materials remained on the wheel surfaces used to grind Ti-20%Ag and Ti-Cu. Qualitative examination with EPMA/WDS showed either titanium and silver or
titanium and copper in the powder. There was no clear difference in the appearance of the wheel surface among the metals tested after grinding at the low speed.

**Young's modulus**

Young's modulus of the alloys is summarized in Fig. 8. As the concentration of silver increased, the Young's modulus decreased. The Young's modulus of the Ti-10%Ag and Ti-20%Ag was significantly lower ($p<0.05$ and $0.001$, respectively) than that of the titanium. On the other hand, it increased as the concentration of copper increased. The Young's modulus of the Ti-5%Cu and Ti-10%Cu was significantly higher ($p<0.01$) than that of the titanium. The Ti-10%Cu had the highest and Ti-20%Ag exhibited the lowest Young's modulus among the metals tested. The Young's modulus of the Ti-Ag alloy had a negative correlation ($r<-0.7$) with the grinding rate values at 1500 m·min$^{-1}$, while that of the Ti-Cu alloy had a positive correlation ($r>0.7$).

**DISCUSSION**

**Grindability**

End milling is commonly applied to CAD/CAM systems. However, sophisticated equipment is needed for machinability evaluation by constant feed rate cutting as performed in industry$^{3-5}$. In dentistry, constant force grinding is often conducted using simple devices to evaluate machinability or tool performance$^{10-17}$. Carborundum wheels, which are generally inexpensive compared with other cutting or grinding tools, were used in this study. Although there are differences in tool material or processing speed, grinding is essentially the same process as cutting$^8$. A work material is removed by many random-shaped small cutting edges on a surface.
The experimental alloys with a higher concentration of alloying elements exhibited a higher grinding rate than did titanium ground at a higher speed. At 1500 m·min⁻¹, the grinding rates of the Ti-20%Ag and Ti-10%Cu alloys were about 2.9 and 2.5 times larger than that of the titanium, respectively. If grindability is independent of grinding speed or time, the rate will be in proportion to the speed, namely the distance that the wheel circumference travels on the surface of the specimen per unit of time. However, the increase in the grinding rates of Ti-20%Ag, Ti-5%Cu, and Ti-10%Cu were greater than the increase in the ratios of speed ground to 500 m·min⁻¹. This relationship signifies that the grindability of the experimental titanium alloys is dependent on the grinding speed and improves at higher speed.

The variations of the grinding rates tended to increase at the higher speed. One possible explanation for this phenomenon is that the wheel may have bounced away from the specimen intermittently, producing a short lapse during grinding, since the carborundum wheel is not a geometrically perfect circle with a hole in the true center. Sparking was observed when grinding the Ti-20%Ag, Ti-5%Cu, and Ti-10%Cu alloys at the higher speeds, which can be attributed to the grinding heat and metal powder. The grinding temperature increased as the grinding speed became higher⁸,³⁶). A considerable number of minute metal particles, which are more combustible than larger metal chips, were generated when the alloys were ground at high speed⁶,³⁷).

A material has poor grindability when tool wear is high, even if the material is removed easily and the grinding rate is high. Evaluation of the grinding ratio is effective for this reason¹⁶). The grinding ratios of the experimental alloys were equal to or higher than that of the titanium. The significantly higher ratios of Ti-20%Ag and Ti-10%Cu at high speeds indicated that the wear of the wheels was low, yet the alloys were readily ground. Adhesion of metal on the ground surface of Ti-20%Ag, Ti-5%Cu, and Ti-10%Cu was more moderate than on the titanium ground at high speed. From these results, it may safely be said that these alloys are more suited for high-speed grinding than titanium. It is certainly predictable that the grindability of the experimental alloys will be improved when wet ground with abundant cutting fluid to lower the grinding temperature⁴−⁹).

**Mechanical properties and grindability**

The strength and hardness of Ti-Ag and Ti-Cu were higher than of the titanium²⁵). The tensile strength of Ti-20%Ag was about 1.6 times greater than that of the titanium. The tensile strength of Ti-5%Cu and Ti-10%Cu was more than twice as high as that of the titanium. It seems reasonable to suppose that a material with high strength or hardness is difficult to machine³⁸). However, the experimental alloys exhibited higher grindability than the titanium, in spite of their higher strength and hardness. By analysis of correlation, the hardness and tensile strength of the Ti-Ag or Ti-Cu alloys had a positive correlation \((r>0.7)\) with the grinding rate values at 1500 m·min⁻¹. It is obvious that the machinability of a material cannot simply be
The elongation of the Ti-Ag alloys became gradually lower than that of the titanium (36%) as the concentration of silver increased; the value for the Ti-20%Ag alloy was about 19%. The elongation of the Ti-Cu alloys decreased as the concentration of copper increased. Ti-5%Cu showed more than 5% elongation, while that of the Ti-10%Cu alloy was no more than 1%. These results were thought to be produced by solid-solution strengthening and by precipitation of the brittle intermetallic compounds as the concentration of the alloying elements increased. The large plastic deformation of a work material can be a cause of high cutting force, high cutting temperature, and long chip length. The elongation of the Ti-Ag and Ti-Cu alloys had a negative correlation \((r<-0.7)\) with the grinding rate values at 1500 m/min. The reduced ductility of the experimental alloys coincides with the finer-sized metal chips.

Elastic modulus of titanium varies through alloying. As the concentration of the alloying element increased, the Young’s modulus of the Ti-Ag alloy decreased, while that of the Ti-Cu alloy increased. Young’s modulus seemed to have no relation with grindability in the present study. However, it is said that the relatively low Young’s modulus of titanium causes chatter vibration or deformation of the workpiece during machining, which often brings about surface imperfections or low machining accuracy. From this point of view, the Ti-Cu alloys, which exhibited higher Young’s modulus than did the titanium, are more favorable for machining than the Ti-Ag alloys.

**Microstructure and grindability**

Industrial free-machining titanium alloys contain sulfur and rare earth metals that produce globular sulfide inclusions to improve machinability. In the steel industry, it is common to improve machinability by adding sulfur to decrease ductility. Industrial free-machining aluminum alloys and free-machining brass generally contain a small amount of low melting temperature elements, which rarely form a solid solution with the matrix. These elements are dispersed in the metal as elements or as a compound, and reduce the ductility of metals. Inclusions in the matrix seem to be a common factor contributing to better grindability. As mentioned above, the experimental titanium alloys have a eutectoid point of \(\alpha\)-Ti and an intermetallic compound (Ti2Ag or Ti2Cu). In previous studies, intermetallic compounds were found in the Ti-20%Ag and Ti-10%Cu. It is possible that the precipitation of Ti2Cu in Ti-5%Cu was not confirmed by EPMA with WDS or X-ray diffraction in the previous studies because the amount of Ti2Cu was very small. A reason for the improved grindability of Ti-20%Ag, Ti-5%Cu, and Ti-10%Cu is the precipitation of the brittle intermetallic compounds. It is known that the mechanical properties of Ti-Cu and Ti-Ag alloys can be varied through controlling the precipitation of Ti2Cu or Ti2Ag intermetallic compounds by heat treating with the eutectoid transformation. The machinability of the Ti-Ag and Ti-Cu alloys can potentially be improved by controlling the precipitation of the intermetallic compounds.
**Melting temperature, chemical reactivity, and grindability**

According to the phase diagrams, the melting temperature of the Ti-Ag or Ti-Cu alloys decreases as the silver or copper concentration increases\(^{33,34}\). The melting temperatures of 20% Ag and 10% Cu alloys are estimated to be 1600°C and 1540°C, respectively, while that of titanium is 1670°C.

The degree of chemical reactivity of a work material is related to the surface finish of the workpiece and the tool life\(^{3,16,49}\). A titanium surface freshly exposed by grinding has great reactivity\(^{50,51}\) and adhesiveness\(^{52}\). When titanium is ground by carborundum (SiC), oxidization and carbonization of the titanium are believed to occur\(^{10,12}\). The former causes discoloration of the ground surface\(^{12,13}\).

When titanium is alloyed, its activity decreases as the mole fraction of titanium in the alloy decreases\(^{31,53}\). It was assumed from the calculation of the standard free energy change of formation of titanium oxides that the chemical reactivity of titanium with oxygen slightly decreases as the concentration of alloying elements increases\(^{31}\). It is conceivable that the chemical reactivity of titanium with carbon decreases as the concentration of alloying elements increases. Judging from the adhesion observed on the ground surfaces and the grinding ratios, the surface finish and tool life of the experimental alloys were improved, or at least were not worse, compared with the unalloyed titanium. However, the grinding burn typically found on titanium resulting from high-speed grinding was not completely restrained by alloying in the present study.

**Thermal conductivity and grindability**

The low thermal conductivity of titanium is thought to be one reason for its poor machinability\(^{3-9,14}\). Assuming that other conditions are equal, the low thermal conductivity of a material inhibits dissipation of heat and results in high tool temperature, generally leading to shorter life of the tool\(^{54}\). The thermal conductivity of titanium at room temperature is 21.9 W·m\(^{-1}\)·K\(^{-1}\)\(^{55}\). On the other hand, silver and copper are known as the most heat-conducting metals. Their thermal conductivity is 428 W·m\(^{-1}\)·K\(^{-1}\) and 398 W·m\(^{-1}\)·K\(^{-1}\), respectively, which is more than 18 times larger than that of titanium\(^{56,57}\). It is feasible that the thermal conductivity can be improved by alloying titanium with silver or copper, and thus, machining will be facilitated. The titanium alloys on the market, however, are reported to possess lower thermal conductivity than titanium\(^{55}\). The thermal conductivity for Ti-2.5%Cu is reported to be 13 W·m\(^{-1}\)·K\(^{-1}\), only about 60% of titanium\(^{56}\). Although the thermal conductivity of the experimental alloys was not measured in the present study, it is quite possible that their values were lower than that of titanium. Assuming that this is true, it can be said that the grindability of the alloys under the present grinding conditions was not significantly adversely affected by their thermal conductivity, since the grinding rates and the grinding ratios of the alloys were the same as or better than those for the titanium.
CONCLUSION

The Ti-20%Ag, Ti-5%Cu, and Ti-10%Cu alloys turned out to possess better grindability than did unalloyed titanium, particularly at high grinding speed. The Ti-Cu alloys showed higher grindability at a lower concentration of the alloying element than did the Ti-Ag alloys. A decrease in elongation caused by the precipitation of small amounts of intermetallic compounds (Ti$_2$Ag or Ti$_2$Cu) was thought to primarily contribute to the grindability of the experimental alloys. Considering the elongation required for dental use, Ti-20%Ag and Ti-5%Cu are good candidates for dental machining alloys.

ACKNOWLEDGMENTS

We are grateful to Sumitomo Sitix Co. Ltd. for providing the high purity titanium sponge. We also thank Mrs. Jeanne Santa Cruz for editing the manuscript.

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