



THE EFFECT OF GRAIN REFINERS IN 18 KARAT YELLOW, PINK, & WHITE GOLD

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INTRODUCTION

Earlier work has been carried out in 14K yellow gold, where various grain refiners were used. Iridium, ruthenium, indium, cobalt and zirconium are among the well-established elements known to have grain refining effects on the 14K gold alloys.¹ Debatable outcomes of grain refinement were achieved when cobalt was used as a grain refiner. Dieter Ott, in a Santa Fe Symposium® paper in 1997, briefly discussed that cobalt has a strong effect on grain refinement in 18K gold under annealed conditions, and has somewhat limited effect in the as-cast state.² Heiner Lichtenberger proved the sound effect of cobalt on refining grains of 10KY and 14KY in a 1995 Santa Fe Symposium paper.³ Dieter Ott showed the influence of grain refiners at relatively higher concentration (ruthenium - 0.1% in 18K and cobalt - 0.5% in 18K) on as-cast 18K yellow gold. We elected to study the effects of iridium, ruthenium, and cobalt at very small addition levels on as-cast pieces. This study solely focuses on the effect of grain refiners on 18K gold made by investment casting in a vacuum casting machine, and it acknowledges the fact that a similar study performed on poured ingot may lead to different outcomes as the rate of solidification changes.

1.1 Regular grains vs refined grains

Grain size plays a vital role in the behavior of a material against any applied stress; depending on the grain size, mechanical properties change. The grains within a microstructure are generally categorized as coarse grains and fine grains. The terms are used in relative manner.⁴ It is generally believed that finer grains are

more desirable in most cases as they require a higher value of stress to plastically deform and eventually fracture the material in normal working conditions. The well-known Hall-Petch equation strengthens the argument favoring fine grains. In that equation, shown below, σ_y is the yield stress, σ_0 is friction stress, k is the constant of the material, and d represents the average grain diameter. The stress required to deform the metal over its elastic limit is inversely proportional to the square of the grain size; fine grains provide more yield strength to the material.

$$\sigma_y = \sigma_0 + kd^{-1/2}$$

1.2 Metal composition

Three 18K color series (yellow, pink, white) were covered in this research, with four different alloys tested in each color series. One out of four alloys in each color series was made with base elemental composition, and the other three alloys were made with the addition of a single but different grain refiner. The amount of added grain refiner was introduced to the expense of copper. The basic alloy composition in our yellow gold and pink gold examples includes silver, copper, and zinc. The white gold examples contained nickel in addition to the three common elements used in yellow gold and pink gold. This paper does not discuss the effect of grain refiners in 18K palladium white gold.

Based on past research on 14K yellow gold, the level of iridium and ruthenium in alloys was kept at 0.1%.¹ Since cobalt does not show any effect at this low level, 0.3% of the total weight of an alloy was used to achieve the desired grain refining effect in the final 18K product.¹

Silicon and boron are commonly used deoxidizers (de-ox) in the jewelry industry. McCloskey discussed that silicon promotes grain enlarging and prevents effective grain refining.⁵ Normandeau explained in a 1996 paper that the addition of silicon up to 0.025% in 18K yellow gold provides benefits, and, on the contrary, destroys metallic behavior when added above 0.05% in 18K yellow gold.⁶ Keeping these acceptable levels of silicon for 18K yellow gold in reference, 0.025% of total de-ox was added in all three colors of the 18K gold. All the experimental 18K gold in this research had just enough de-ox to maintain fluidity and achieve a clean casting surface,⁷ but it did not exceed a level where it creates counteractive action of grain refining.⁶

The following table lists the metal composition used for this study. This paper recognizes that the results may change even with a

slight adjustment in base metal composition. The paper will use the sample ID as a point of reference.

Table 1: Metal composition of yellow gold, pink gold & white gold

Color Series	Sample ID	Nominal metal composition in %							
		Au	Ag	Cu	Zn	Ni	Ir	Ru	Co
Yellow	1Y	75.00	11.00	13.500	0.50	-	-	-	-
	2Y	75.00	11.00	13.475	0.50	-	0.025	-	-
	3Y	75.00	11.00	13.475	0.50	-	-	0.025	-
	4Y	75.00	11.00	13.425	0.50	-	-	-	0.075
Pink	1P	75.00	2.25	22.250	0.50	-	-	-	-
	2P	75.00	2.25	22.225	0.50	-	0.025	-	-
	3P	75.00	2.25	22.225	0.50	-	-	0.025	-
	4P	75.00	2.25	22.175	0.50	-	-	-	0.075
White	1W	75.00	5.00	13.250	2.25	4.50	-	-	-
	2W	75.00	5.00	13.225	2.25	4.50	0.025	-	-
	3W	75.00	5.00	13.225	2.25	4.50	-	0.025	-
	4W	75.00	5.00	13.175	2.25	4.50	-	-	0.075

2. Casting Procedure

Conventional wax was used to build pattern trees, as shown in Figure 1. The design of the trees was kept identical for all the castings to avoid any weight and geometry discrepancies. The shown patterns were invested using Prestige Optima investment with a water-to-powder ratio of 39/100 under vacuum for four minutes. The molds were then put into an electric oven for a complete burnout of the wax. Mixing and pre-alloying (gold + alloy) were done under an argon cover to create homogenous casting grains using a Neutec JZP machine. Once pre-alloyed, a melting range test was performed using Differential Scanning Calorimetry (DSC) for all 18K gold to achieve an optimum temperature to cast these metals. The same Neutec JZP machine was used to cast. Figure 2 shows the appearance of each casting after removal of investment using a pickle solution.



Figure 1: Wax model of casting tree



Figure 2: Castings appearance after investment removal

3. Microstructure Evaluation

The test samples to evaluate microstructure were made of 1 cm x 1 cm square with 0.2 cm thickness. The microstructure was evaluated on the edge of each sample, as shown in Figure 3. These samples were cold-mounted and polished using the standard metallographic technique.



Figure 3: Mounted sample of 1Y for microstructure analysis

These samples were etched using 1:1 ratio of hydrochloric acid (HCl) and chromic acid (H₂CrO₄) to reveal the grain structure. Using an inverted optical metallograph, these samples were examined up to 100X. The intercept method was used to measure the grain size. Table 2 shows the grain size revealed by each sample after etching. All the microstructure images are presented at 50X

magnification in this paper for better visualization of the grains, because precious metals have relatively larger grain size compared to ferrous and other non-ferrous metals. Table 3 shows the conversion of ASTM grain size numbers to average grain diameter calculated at 100X.

Table 2: Calculated grain size per ASTM E112-13

Sample ID	Sample Description	ASTM Grain Size No.
1Y	18KY	0
2Y	18KY with Iridium	1.5
3Y	18KY with Ruthenium	0
4Y	18KY with Cobalt	Coarser than 00
1P	18KP	Coarser than 00
2P	18KP with Iridium	0
3P	18KP with Ruthenium	0.5
4P	18KP with Cobalt	Coarser than 00
1W	18KW	1.0
2W	18KW with Iridium	1.5
3W	18KW with Ruthenium	1.5
4W	18KW with Cobalt	0.5

Table 3: Conversion of ASTM grain size number to average grain diameter per ASTM E112-13

ASTM Number	Average grain diameter (μm)
00	508.0
0	359.2
0.5	302.1
1	254.0
1.5	213.6

3.1 Discussion of 18KY microstructure

Figures 4-7 represent the microstructure of the as-cast polished samples of 1Y, 2Y, 3Y, and 4Y, respectively. The pictures shown below represent the area captured under 50X magnification. The grain size of the regular yellow gold (1Y) here is ASTM 0. The microstructure of sample 2Y indicates that iridium made the grains smaller. On the other hand, cobalt tends to enlarge the grains from their original grain size, as shown in Figure 7, representing the sample 4Y. Figure 6, showing sample 3Y, indicates that ruthenium made a slight impact in refining the grains. Even though Figure 6

shows some smaller grains, the calculated ASTM grain size stays at 0 for sample 3Y. Figures 5 and 7 clearly acknowledge that iridium and cobalt have the opposite effect on the grains of 18KY. Sample 2Y falls at ASTM 1.5, and sample 4Y falls at coarser than 00. These numbers suggest that 0.075% of cobalt in 18K gold does not refine the grains and that ruthenium has almost negligible effect.

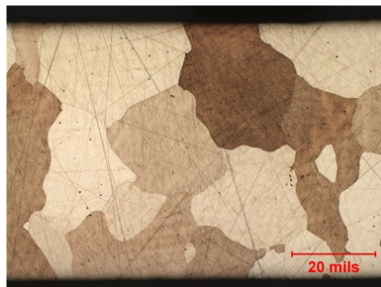


Figure 4: Photomicrograph showing the grain structure of 1Y (regular), HCl-chromic acid etch, 50X original magnification

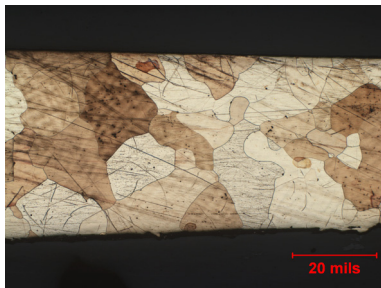


Figure 5: Photomicrograph showing the grain structure of sample 2Y (iridium), HCl-chromic acid etch, 50X original magnification

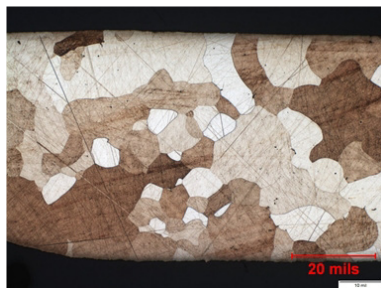


Figure 6: Photomicrograph showing the grain structure of 3Y (ruthenium), HCl-chromic acid etch, 50X original magnification

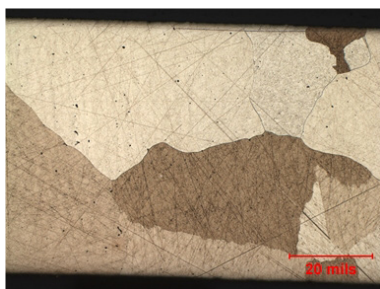


Figure 7: Photomicrograph showing the grain structure of 4Y (cobalt), HCl-chromic acid etch, 50X original magnification

3.2 Discussion of 18KP microstructure

The ramification of refinement in pink gold is shown in Figures 8-11. All these images were captured at 50X magnification. The grain size calculation shows that regular pink gold (1P) has a grain size coarser than ASTM 00. Figures 9 and 10 clearly show the average grain size is smaller in samples 2P and 3P, compared to sample 1P, shown in Figure 8. The grain size of sample 4P suggests a negligible change in the grains, as represented in Figure 11. Just like yellow gold, iridium makes grain size smaller. In contrast to yellow gold, it is evident from Figure 10 that ruthenium has strong refining effect on pink gold. The grain size in sample 2P changes to ASTM 0, and the sample 3P shows that the grain size is ASTM 0.5. However, the grain size of sample 4P stays coarser than ASTM 00, which means cobalt does not refine the grains at 0.075% of the total 18K weight. Iridium and ruthenium both have an effect in making grains small at the addition of 0.025% of the total 18K gold.

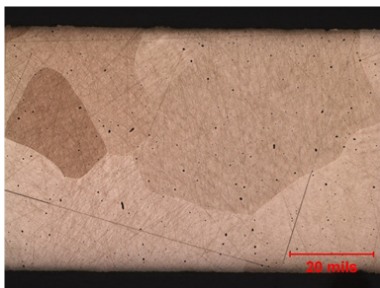


Figure 8: Photomicrograph showing the grain structure of 1P (regular), HCl-chromic acid etch, 50X original magnification

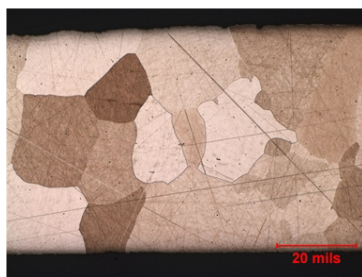


Figure 9: Photomicrograph showing the grain structure of 2P (iridium), HCl-chromic acid etch, 50X original magnification

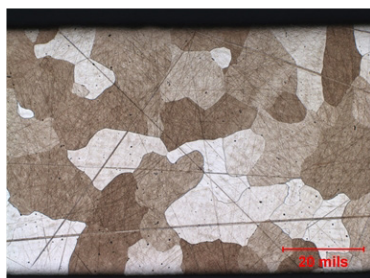


Figure 10: Photomicrograph showing the grain structure of 3P (ruthenium), HCl-chromic acid etch, 50X original magnification

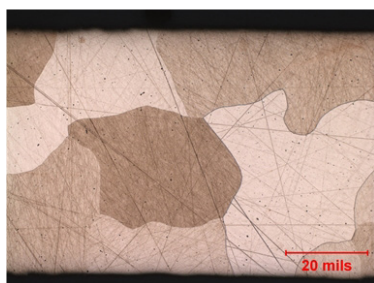


Figure 11: Photomicrograph showing the grain structure of 4P (cobalt), HCl-chromic acid etch, 50X original magnification

3.3 Discussion of 18KW microstructure

The change in grain size in white gold with the addition of the grain refiners is represented in Figures 12-15. All the images presented here are at 50X magnification. The grain size of regular white gold (1W) without any grain refiner stands at ASTM value of 1. It is safe to state that white gold grains are smaller compared to yellow gold and pink gold. Looking at Figures 13 and 14, it is

difficult to judge which grain refiner, iridium or ruthenium, works better in white gold. They both appear to equally make the grains smaller; ASTM grain calculation report strengthens this position. For sample 2W and 3W the grain size shifts from ASTM 1 to ASTM 1.5. Just like yellow gold and pink gold, cobalt does not refine white gold. Cobalt addition tends to coarsen the grains from ASTM 1 to ASTM 0.5. Table 2 and Figures 12-15 prove that at 0.025% of the total weight, iridium and ruthenium make the grain small, whereas 0.075% of cobalt does not.

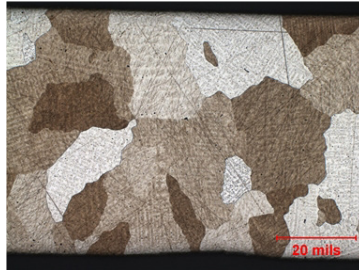


Figure 12: Photomicrograph showing the grain structure of 1W (regular), HCl-chromic acid etch, 50X original magnification



Figure 13: Photomicrograph showing the grain structure of 2W (iridium), HCl-chromic acid etch, 50X original magnification

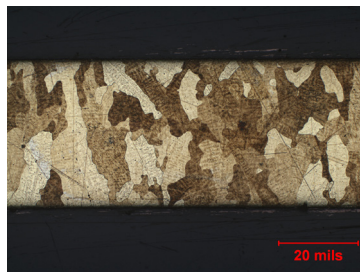


Figure 14: Photomicrograph showing the grain structure of 3W (ruthenium), HCl-chromic acid etch, 50X original magnification

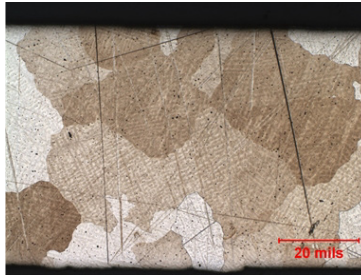


Figure 15: Photomicrograph showing the grain structure of 4W (cobalt), HCl-chromic acid etch, 50X original magnification

4. Vickers Hardness

Hardness is the measure of a material's resistance to plastic deformation (permanent deformation) against a localized stress. Precious metals including gold, silver, platinum, and palladium are very soft by nature. Since the jewelry industry primarily deals with precious metals, the hardness becomes an important aspect for material selection. It is believed that the harder the metal, the easier it is to polish. Apart from some applications such as handmade jewelry, dealing with complicated prong work, or certain fabrication processes, harder metals are generally preferred.

Vickers hardness is one of the techniques for measuring this unique mechanical property of materials. Rockwell and Brinell are other widely used hardness methods. This technique was invented by Robert L. Smith and George E. Standland at Vickers Ltd. This method uses a diamond indenter to make an impression on a material surface. Figure 16 shows what an indent looks like. At any identical load and dwell time, the smaller the indent the harder the material. A larger indent indicates lower resistance against the localized stress and, thus, softer material. Usually, the surface on which the indentation process is carried out needs to be flat. The calculation is carried out by using the following equation, where F — force, N; and d — indentation diagonal, mm.

$$HV = 0.1891 \frac{F}{d^2}$$



Figure 16: Impression of an indentation on the 18KY gold surface

4.1 Hardness sample preparation and testing

The ASTM E384-22 standard was followed in performing micro-hardness testing. The test samples were made of 1 cm x 1 cm square with 0.2 cm thickness. All the samples were cold-mounted on a flat surface, followed by standard metallographic grinding and polishing technique. Once all the samples were mirror polished, they were tested with a Vickers microhardness tester. A 100-GF (gram force) of the load was applied for 11 seconds on all the samples to determine the HV number. The tests were performed in the center region of the sample to avoid catching the work-hardening effect around the edges, which may have occurred due to cutting the samples from the casting tree. Figure 16 shows an indent on sample 1Y. Five readings were taken on each sample, and an average was calculated to represent the HV value.

4.2 Hardness results discussion

The average hardness value of the yellow gold, pink gold, and white gold is represented using a line chart in Figures 17, 18, and 19, respectively. Each line chart shows how the hardness value changes with the addition of a grain refiner. As shown in Figure 17, the hardness of 18K yellow gold is hardly affected with an addition of the grain refiner. In 18K pink gold, two out of three grain refiners work well. The average hardness value goes from 195 HV to 210 HV with the addition of cobalt, whereas it moves to 211 HV with the help of ruthenium. The difference of 15 HV can be considered significant with the base value of 195 HV. Figure 18 shows iridium only moves hardness value to 198 HV. As far as 18K white gold is concerned, the hardness value increases only a few points when cobalt is added as a grain refiner (Figure 19). Iridium and ruthenium do not show any positive difference in the hardness value of the white gold. On the contrary, they bring the HV value down even though the grain size has actually reduced.

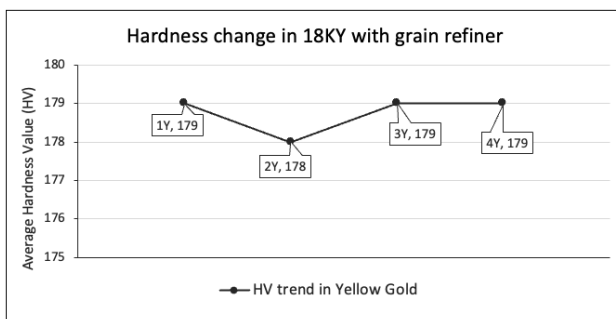


Figure 17: Trend of average hardness value in yellow gold with different grain refiners

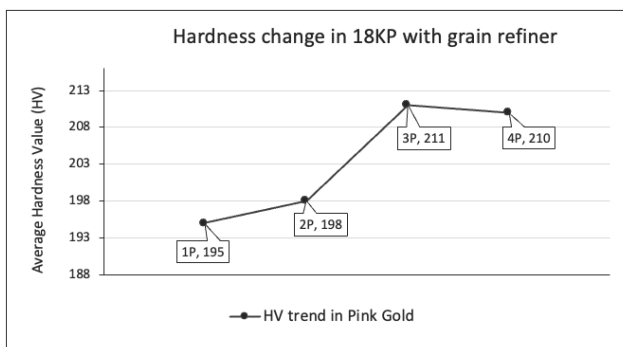


Figure 18: Trend of average hardness value in pink gold with different grain refiners

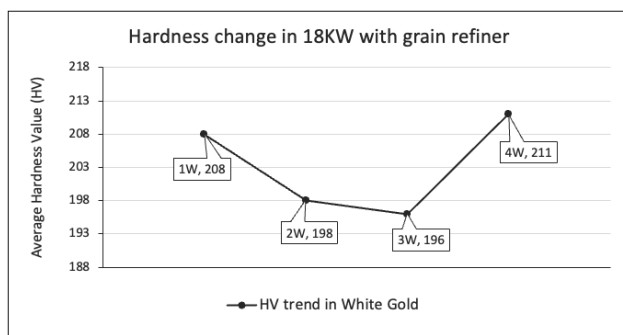


Figure 19: Trend of average hardness value in white gold with different grain refiners

5. Tensile Testing

Tensile testing is one of the most important test methods to understand some of the key mechanical properties of any material. Fundamental behavior of materials, such as yield strength, tensile strength, and ductility, are defined by this test. Figure 20 represents the stress-strain curve under tension. The yield-strength point in the stress-strain diagram represents the ability of any material to regain its shape under applied force (stress). When the stress is above this point, the material cannot regain its original shape and it enters a permanent deformation zone.

In the jewelry industry, understanding this property becomes imperative as it allows for the proper selection of metal according to a specific need. The line between the yield strength and fracture point is known as the plastic zone of the material. The higher the line area, the more ability to stretch/pull the material before it completely fails. This property is very desirable for hand-making and fabrication applications. If the metal does not tolerate much stress between the yield point and fracture point, that metal will be less likely to be useful in chain- or wire-making, as it will fracture easily. Sections 5.1-5.3 discuss in detail how adding grain refiner changes some of these properties, including yield strength, elongation, and the ultimate tensile strength (UTS). The ASTM E 8-24 method was used to carry out tensile testing of 18K gold samples. Yield strength was determined by the 0.2% offset method.

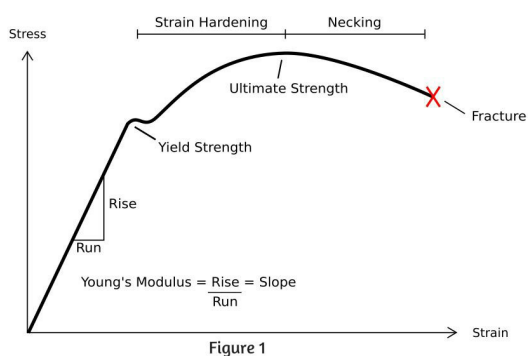


Figure 20: Stress-strain diagram defining material properties

5.1 Tensile test in 18KY gold

The column bars represented with horizontal lines in Figures 21-23 provide details on how 18KY performed when put under tensile stress. The bars in Figure 21 represent the yield-strength value of

18KY gold samples. The yield strength of regular yellow gold (1Y) is 43 ksi. The yield strength of sample 2Y with iridium and 3Y with ruthenium is very close to the regular yellow gold at 41.2 ksi and 41 ksi, respectively. The bar of 4Y shows that cobalt brings the value down from 43 ksi to 39.15 ksi.

The bars in Figure 22 represent the UTS value of yellow gold. The UTS value of regular gold (1Y) is 57 ksi. The UTS of sample 3Y with ruthenium stays the same as sample 1Y at 57 ksi. However, samples 2Y with iridium and 4Y with cobalt show a decrease in the UTS value to 55 ksi and 49.5 ksi, respectively.

The bars in Figure 23 show elongation in percentage. The regular yellow gold (1Y) shows 54% elongation. Sample 2Y with iridium shows a drop in elongation from 54% to 48%, and 3Y with ruthenium shows negligible change in elongation with 53%. Sample 4Y, made with cobalt, clearly showed that it only elongated up to 39% compared to the other yellow gold samples where elongation is higher. Looking at all three findings, it is safe to assess that this study shows that the tensile properties of 18KY gold are marginally altered by iridium (0.025 wt.%) and ruthenium (0.025 wt.%), whereas cobalt (0.075 wt.%) weakens the tensile properties as expected from its ASTM grain size number.

5.2 Tensile test in 18KP gold

The solid black column bars in Figures 21-23 provide details on how 18KP performed when put under tensile stress. The yield strength of regular pink gold (1P) is 47.4 ksi. The yield strength of sample 2P with iridium stays very close to sample 1 at 46.5 ksi. Sample 3P shows that ruthenium takes the yield strength value to 49.5 ksi. Like yellow gold, cobalt brings this value down significantly to 43.5 ksi as per the 4P bar.

The bars in Figure 22 suggest that sample 3P with ruthenium increased tensile strength to 62 ksi from 52 ksi of regular pink gold sample 1P. Sample 2P with iridium shows a slight increase in the ultimate tensile strength (UTS) value to 52.5 ksi, and 4P with cobalt shows a decrease in the value to 50 ksi.

Even though the samples containing iridium and cobalt do not show a significant shift in yield strength and tensile strength, they indeed show a difference in elongation. The bars in Figure 23 indicate that all the grain refiners helped increase the ductility of the pink gold. The elongation of 2P (33%), 3P (34%), and 4P (34%) is more than double compared to sample 1P (16%). Looking at all three characteristics together, it is evident ruthenium

(0.025 wt.%) is the most successful grain refiner in improving the tensile properties of 18K pink gold.

5.3 Tensile test in 18KW gold

The cross-hatch column bars in Figures 21-23 provide the details on how 18KW performed when put under tensile stress. As shown in Figure 21, the regular white gold (1W) has a yield strength of 55.5 ksi. Sample 2W with iridium and 4W with cobalt positively shift the yield strength value to 57.5 and 58.25 ksi respectively. Sample 3W with ruthenium is showing a drop at 52 ksi.

The bars in Figure 22 show an upward shift in the UTS value of white gold containing iridium and cobalt. The UTS value of samples 2W and 4W moves to 69.5 ksi and 69.75 ksi, respectively, from the original value of 62.5 ksi in the regular white gold sample 1W. The UTS value in sample 3W containing ruthenium goes down to 61.5 ksi.

The elongation percentage shown in Figure 23 shares key information. Iridium and cobalt bring more ductility to white gold. The regular white gold sample 1W was only elongated 36% followed by the sample 3W with ruthenium at 37%. However, samples 2W and 4W had elongations of 46.5% and 45.5%. Looking at all results, it is safe to conclude that iridium (0.025 wt.%) and cobalt (0.075 wt.%) are more effective in improving the tensile properties of white gold, whereas ruthenium (0.025 wt.%) is less effective and keeps the values more or less the same.

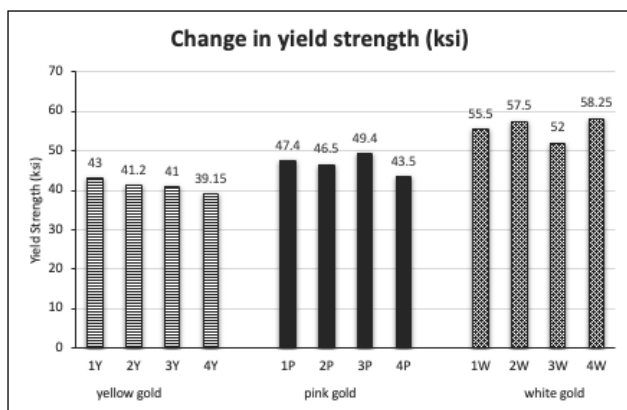


Figure 21: Change in yield strength of yellow gold, pink gold & white gold (left to right) with different grain refiners

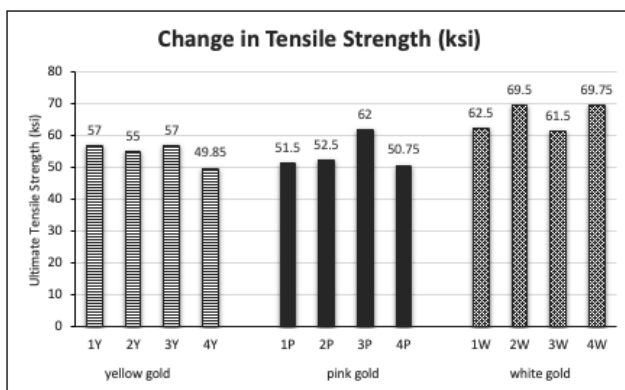


Figure 22: Change in tensile strength of yellow gold, pink gold & white gold (left to right) with different grain refiners

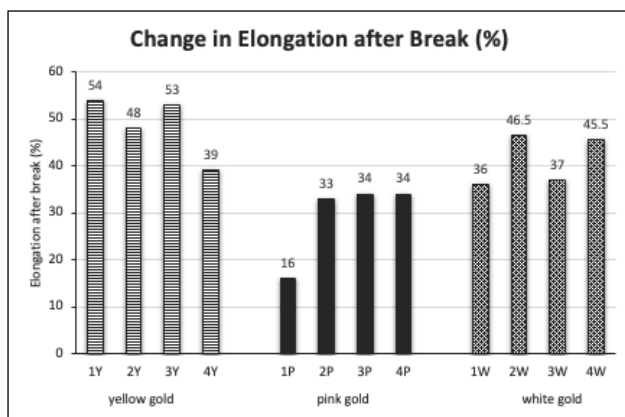


Figure 23: Change in elongation after break of yellow gold, pink gold & white gold (left to right) with different grain refiners

CONCLUSIONS

Based on results, the following conclusions can be made.

1. Out of all three colors, yellow gold was the least influenced by the grain refiners in our study. The ASTM grain size number and microstructure suggest that iridium is successful in refining 18KY gold grains. However, the hardness and tensile tests suggest that there is no considerable difference in mechanical properties. Ruthenium has no effect on the yellow gold grains. Cobalt increased the grain size and, at the same time, also weakened the tensile properties with no change in hardness.
2. Ruthenium converts the grain size of the original 18KP from ASTM coarser than 00 to ASTM 0.5, increasing the hardness

and improving the tensile properties. Even though iridium makes some improvement in grain size, it does not really change the mechanical properties of 18K pink. Cobalt neither refines nor coarsens the pink gold grains but raises the hardness values.

3. It is evident that iridium not only refines the 18KW gold grains but also improves their tensile properties. Even though cobalt made the grain structure coarser, it has improved all the mechanical properties. Ruthenium refines the grains, but it has a negligible effect on the tensile properties of 18KW gold, decreasing the hardness.

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