The Metallurgy of Some Carat Gold Jewellery Alloys

PART II — NICKEL CONTAINING WHITE GOLD ALLOYS

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The first part of this article detailed the relationships existing between the composition, metallurgical structure and properties of coloured jewellery gold alloys. In this second part, the same treatment is applied to nickel containing white gold alloys.

Most commercial white gold alloys used in North America are based on the gold-copper-nickel or the gold-copper-nickel-zinc system. In other parts of the world, alloys in which palladium is substituted for all or part of the nickel are also used. The latter will, however, not be discussed in this article.

The Metallurgical System

If the gold-copper-nickel system is approached as was the gold-silver-copper system by considering the three binary phase diagrams gold-nickel, nickel-copper, and copper-gold in Figure 8, the solid state immiscibility field in the nickel-gold system would be expected to intrude into the ternary field and, indeed it does, as shown in Figure 9. If Figure 9 is compared with Figure 3 in Part I, it will be seen that the systems are similar but are differently orientated with respect to gold. In the gold-silver-copper system, the two-phase field extends from the side opposite the gold corner, whereas in the gold-copper-nickel system, the two-phase field extends from the side opposite the copper corner. Thus, each constant carat level in the gold-silver-copper alloy system falls on a line which cuts symmetrically through the immiscibility field. From a metallurgical point of view, it would be logical to study the gold-copper-nickel system by considering alloys along lines which cut symmetrically through the immiscibility field in Figure 9. Unfortunately, such lines are lines of constant copper content and the alloys along them bear no relation to jewellery alloys. Therefore, the less logical but more pertinent choice of alloys on lines of constant gold content has to be made, although such lines cut asymmetrically through the immiscibility field. On this basis, schematic quasi-binary sections at 18, 14, and 10 carat are shown in Figure 10 with, on the abscissa, a plot of the parameter Cu′ defined as:

$$\mathrm{Cu'} = \frac{\mathrm{Cu\ wt.\%}}{\mathrm{Cu\ wt.\%} + \mathrm{Ni\ wt.\%}} \times 100 \qquad \text{(per cent)}$$

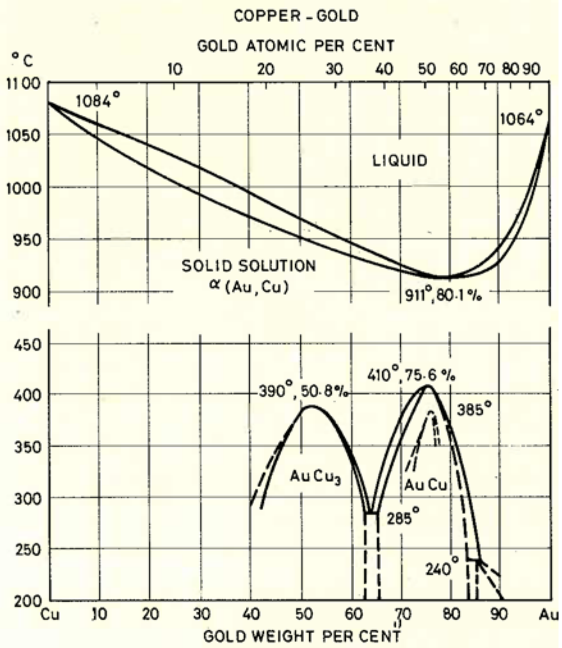
As in the case of coloured gold alloys where the alloys were discussed in terms of three parameters: caratage, Ag′, and zinc content, gold-copper-nickel-zinc white gold alloys will be discussed in terms of three parameters: caratage, Cu′ and zinc content.

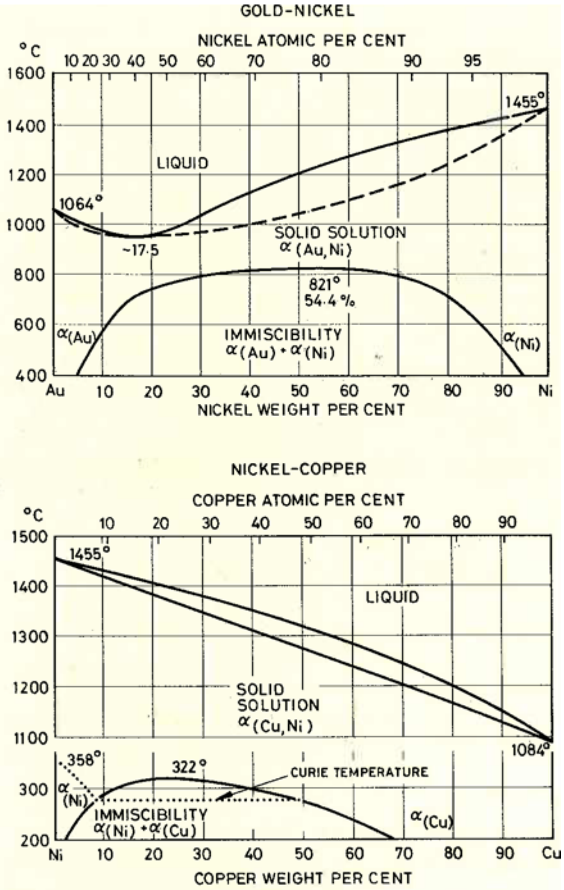
Useful Jewellery Alloys

The area of the ternary system occupied by useful white jewellery gold alloys is far more restricted than in the case of coloured gold alloys. Historically, the present nickel-bearing white gold alloys were derived from alloys introduced in the 1920's as substitutes for platinum for diamond settings. A typical early alloy consisted of 81 gold/16 nickel/3 zinc weight per cent. If this 19½ carat alloy is converted to lower caratage, the workability deteriorates rapidly. At 18 carat, some copper is essential for practical workability and sizeable amounts are needed at 14 and 10 carat. However, there is a limit to the amount of copper that can be tolerated while retaining a white colour. Zinc, which is an ingredient of most nickel-bearing white gold alloys, tends to enhance the whitening effect of nickel and to compensate somewhat for the colouring effect of copper. However, zinc also tends to increase firecracking. That is, when nickel-bearing white gold alloys are lightly worked (less than the equivalent of about 50 per cent reduction in cross section) prior to annealing, cracking may occur at the grain boundaries on annealing. This fact is well known to the industry. The metallurgical reason for the phenomenon has still to be precisely defined.

The compositions of white gold alloys that have evolved over the years are the result of an empirical compromise between these various factors. In Figure

Fig. 8 Gold-nickel, nickel-copper and copper-gold binary phase diagrams. Some comments on the copper-gold diagrams were made in the caption for Figure 1. The existence of a large solid-state immiscibility field in the gold-nickel system has an important influence on the metallurgical properties of ternary gold-copper-nickel alloys. After (1)





11, the areas wherein almost all white jewellery alloys have been made are covered by the bold blocks on the carat lines. The broken lines on the diagram indicate the approximate boundary at which white alloys tend to become yellowish. The gold-nickel binary diagram on the left is included to help the reader visualise the intrusion of the immiscibility field into the ternary diagram.

Discussing the coloured gold alloys, in terms of 'types' depending on carat, Ag′, and zinc content was found convenient. White alloys cannot be ordered as nicely. However, it will facilitate the discussion if the alloys are arranged in the following groups:

Alloy group	Cu′ per cent	Zn wt. per cent
18 ct A:	6 to 11	5 to 6
18 ct B:	31 to 33	5 to 6
14 ct A:	50 to 54	9
14 ct B:	66 to 68	9
14 ct C:	66 to 68	6
10 ct A:	50 to 54	12
10 ct B:	66 to 68	12
10 ct C:	66 to 68	9

In Figure 11 the A alloys occur at the left end of the bold segments at comparatively low values of Cu′ and the B and C alloys occur at the right end at comparatively high values of Cu′. As a rule, the zinc content increases with decreasing caratage. Also at both 14 and 10 carat A, B and C alloys occur within the

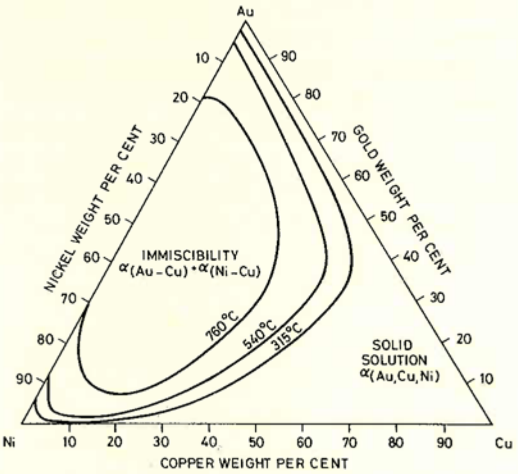


Fig. 9 Projection on the room temperature plane of the gold-copper-nickel ternary phase diagram of some isothermal solid-state boundaries of the immiscibility field. After (9)

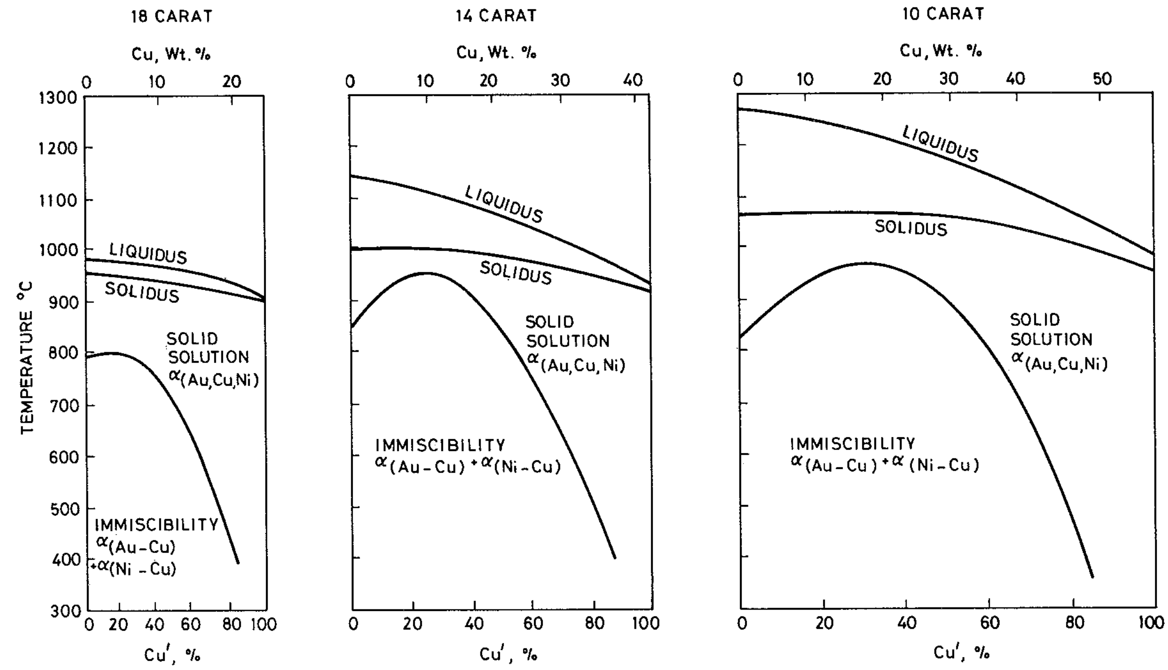


Fig. 10 Schematic quasi-binary sections at constant caratage of the gold-copper-nickel ternary phase diagram. The parameter Cu′ is defined in the text

same overall range of Cu′ values, that is 50 to 68 per cent whereas at 18 carat, the range is much lower at 6 to 33 per cent. At all caratages, the upper limit of Cu′ is determined by the amount of copper that can be tolerated before the white colour becomes yellowish. On the other hand, the lower limit of Cu′ is determined by the metallurgical characteristics of the gold-copper-nickel system.

In the quasi-binary sections in Figure 10, it is clear that as nickel replaces gold in lower carat alloys, the liquidus temperatures rise to values that are not adaptable to jewellery gold casting, also, the alloys move deeper and deeper into the immiscible $\alpha_{(Au\text{-}Cu)} + \alpha_{(Ni\text{-}Cu)}$ region where the alloys have very limited workability. It is for these reasons that in the historical development of low carat white alloys from the early 19½

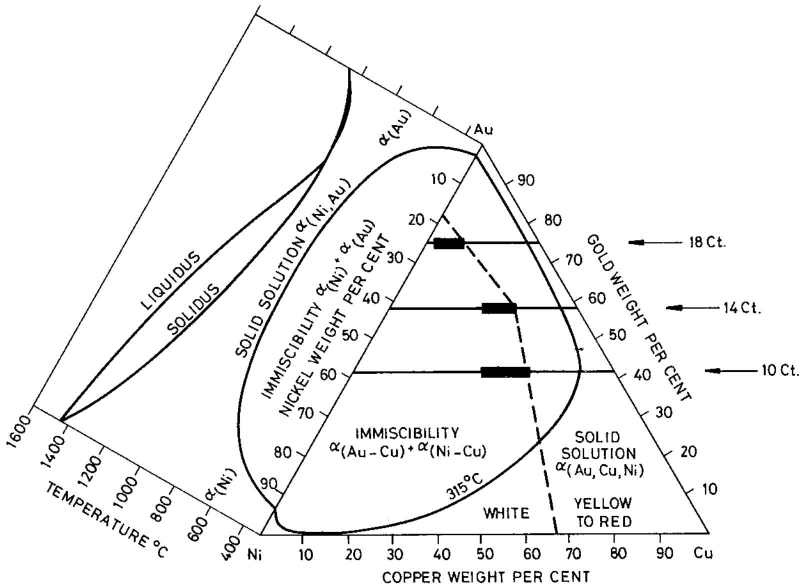


Fig. 11 Relationship between the colour and composition of gold-copper-nickel alloys. Usual jewellery white gold alloys have compositions within the bold segments of the constant caratage lines through the diagram. Thus all such alloys are susceptible to solid-state decomposition into nickel-rich and gold-rich phases

carat silver-nickel-zinc alloy, it was found that some copper was necessary at 18 carat and much more at 14 and 10 carat in order to produce workable jewellery alloys.

The following general statements are of relevance to white gold alloys:

(1) 18 carat A alloys are harder than all other carat gold alloys (coloured or white) whether in the as cast, rolled, annealed, or precipitation hardened condition

(2) 18 carat B alloys are hard in the as cast, rolled and annealed condition, but they are not precipitation hardenable

(3) 14 carat A and 10 carat A alloys are hard in the as cast, rolled and annealed conditions and are not appreciably precipitation hardenable

(4) 14 carat B and 10 carat B alloys are fairly hard (14 ct) to fairly soft (10 ct) in the as cast, rolled and annealed conditions; they are not precipitation hardenable

(5) 14 carat C and 10 carat C alloys are slightly harder than 14 carat B and 10 carat B in the as cast, rolled and annealed conditions and are not precipitation hardenable

At 18 carat, the A alloys are the most popular. The B alloys being richer in copper are less white.

At 14 and 10 carat, the progression of alloys A to B to C is, by and large, in the direction of increasing Cu′ and decreasing zinc content. This has also been the sequence of historical development. The C alloys are the standard alloys today because they combine good workability with minimal firecracking tendencies.

All nickel-based white gold alloys work-harden much faster than coloured gold alloys.

All nickel-based white gold alloys firecrack, but their susceptibility to firecracking varies considerably. A classification of white gold jewellery alloys in order of increasing susceptibility to firecreacking would be:

$$\text{C alloys} \ll \text{B alloys} < \text{A alloy}$$

Thus, high Cu′ values and low zinc contents reduce the susceptibility to firecracking.

All nickel-based white gold alloys are highly segregated after casting. 18 Carat alloys homogenize very readily on working and annealing, 14 carat alloys much less readily, and at 10 carat, the alloys never completely homogenize during normal shop working schedules.

Reference to commercial alloys will ullustrate the above general statements.

Commercial Nickel-Based White Gold Alloys

Listed below are the compositions (weight per cent) and properties of the most common nickel-based white gold alloys sold in North America:

	Au	Cu	Ni	Zn	Cu′
18 ct A	75	2.23	17.3	5.4	11%

Hardness (HR45T)	
As cast	70 to 75
Rolled (50 per cent reduction)	79
Solution annealed	65 to 68
Precipitation hardened	81

The heat treatment schedule for this alloy would consist of solution annealing at 760°C for 1 hour, water quenching and precipitation hardening at 425°C for 30 minutes.

	Au	Cu	Ni	Zn	Cu′
14 ct C	58.3	23.5	12.2	6	66%
10 ct C	41.7	32.8	17.1	8.4	66%

	14 ct	10 ct
Hardness (HR45T)		
As cast	53 to 57	47 to 53
Rolled (50 per cent reduction)	76	76
Solution annealed	50 to 53	40 to 45
Solution annealing temperature (°C)	540 to 650	650 to 760

These two alloys are not precipitation hardenable.

Conclusion

These articles review primarily the gold-silver-copper and gold-silver-copper-zinc coloured alloys and gold-copper-nickel-zinc white alloys used in the United States. The discussion of the gold-silver-copper-zinc system probably covers all coloured alloys fairly well. In the case of white alloys, discussion has been limited to those based on gold-copper-nickel-zinc. White gold alloys can be and have been made using palladium or nickel plus palladium together rather than nickel alone to produce a white colour.

The literature on jewellery golds is so dispersed, spotty, and proprietary that it is difficult to acknowledge the contributions of the many people who have worked in the field. In the case of coloured alloys, however, acknowledgement is made to the early work of L. Sterner-Rainer (4), and in the case of white alloys, to the work of E. M. Wise (5, 6). Extensive bibliographies on jewellery alloys have been prepared by E. M. Wise (7) and E. Raub (8).

References

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