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INTRODUCTION

Cobalt-base alloys have found wide usage in aeronautical applications because of their high strength coupled with generally good oxidation resistance in the intermediate temperature range between approximately 1500° and 2000° F. Such applications include turbojet-engine stator vanes, turbine buckets, and turbine-engine combustion chamber components, to mention a few.

There is also considerable interest in cobalt-base superalloys for use in advanced space power systems. In the latter application, however, material volatility is a major consideration. Furthermore, the property of oxidation resistance, which is usually a matter of the utmost importance in an air environment, becomes of negligible importance in the high vacuum of space. The conventionally used cobalt-base superalloys all contain high (up to 25 percent) percentages of chromium, which has a relatively high evaporation rate in vacuum and which imparts oxidation resistance to these alloys. An investigation is being conducted at the NASA on an entirely different class of cobalt-base superalloys in which low-volatility elements are the primary alloying constituents and the use of chromium is minimized (refs. 1 and 2). In addition to providing desirable properties for space use, these new alloys also appear to be of considerable interest for certain aeronautical applications. This paper describes these alloys and their significant properties.

The importance of low volatility in materials to be used in a space envi-

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ronment can better be understood by consideration of figure 1, which shows the material loss rates of various metals as a function of temperature in inches per 10,000 hours, which represents a space mission of approximately 1 year. These data were compiled from reference 3. For example, at 1800° F, chromium has an evaporation loss rate of approximately 0.030 inch in 10,000 hours, which is clearly undesirable for thin-walled tubing applications in space-vehicle powerplants. Of course, these values are for pure metals, and dilution and other effects will probably exist in the case of alloys. Nevertheless, it appears from the magnitude of these losses that evaporation of volatile alloying constituents cannot safely be ignored. It should be noted here that Russian work (ref. 4), in which the vapor pressures of cobalt and nickel were measured, showed considerably higher values of vapor pressure for these metals than reference 3. Until this discrepancy is resolved, however, reference 3 represents a comprehensive compilation of evaporation data and is considered as the basis for the comparisons that are made herein.

Typical advanced space power systems, in which cobalt-base superalloys might be used, are illustrated in figure 2. The figure shows schematic diagrams of two turboelectric power systems in which nuclear power is converted to electric power through the medium of closed thermodynamic cycles (ref. 5). A heat-transfer fluid is used to extract heat from the reactor and drive a turbogenerator. The Rankine cycle employs a dual loop and uses liquid-metal heat-transfer and turbine-drive fluids, whereas the Brayton cycle employs a single loop and an inert gas as the heat-transfer and turbine-drive fluid.

Cobalt-base alloys are of particular interest if a liquid metal (e.g., mercury or alkali metal) is used as the heat-transfer fluid. Extensive corrosion studies made at the NASA with mercury up to 1300° F for 100 hours have shown nickel-free cobalt-base alloys to be superior to nickel-base and nickel-bearing cobalt-base alloys, although inferior to refractory metals (ref. 6). Only limited corrosion data are available to date with the alkali metals, and extensive research is still required to establish fully the relative merits of various materials with respect to alkali-metal corrosion.

Cobalt-refractory-metal alloys were considered to have attractive possibilities for space-power-system applications in view of some interesting high-temperature strength properties observed by earlier investigators (refs. 7 and 8). A ternary alloy, Co-25W-1Ti, was selected as the basis for systematic alloying studies that initially utilized only low-volatility additives. Subsequent development work also utilized the addition of small amounts of chromium (up to 3 percent), which it was believed would still tend to leave these alloys inherently more resistant to evaporative loss than conventional high-chromium-bearing alloys. All alloys were induction-melted under an argon gas cover. Melts weighed approximately 3 pounds. Vacuum melting is not essential for these alloys but greatly improves the surface appearance of castings.

CHROMIUM-FREE ALLOYS

Stress rupture properties

The two strongest chromium-free alloys developed were Co-25W-1Ti-0.4C and Co-25W-1Ti-1Zr-0.4C. The chemistry generally corresponds to these designations except for zirconium (see ref. 1).

Figure 3 illustrates the as-cast stress-rupture properties at 1800° F in air of these two alloys compared with representative current cast cobalt-base alloys, SM-302 (ref. 9) HS-31 (ref. 10), and WI-52 (ref. 11). It is evident that, although no attempts were made to protect the experimental alloys against oxidation by use of coatings, these alloys compare favorably up to about 700-

hour life with the conventional alloys, all of which contain between 21 and 25 percent chromium.

The rupture strengths of the sheet are somewhat less than those of the cast material. Figure 4 illustrates the sheet stress-rupture properties at 1800° F of the Co-25W-1Ti-0.4C alloy compared with those of two of the strongest current cobalt-base sheet alloys, J-1650 (ref. 10) and L-605 (HS-25, ref. 12). To avoid loss of load-bearing area by oxidation, the thin (0.050-in.-thick) cobalt-refractory-metal-alloy sheet specimens were tested in helium. These data compare quite well with the conventional cobalt-base alloys. Solution treatments were the only heat treatments attempted. It is probable that the properties could be improved by suitable aging or combinations of working and aging.

It should be noted that the experimental alloys have theoretical densities of 0.363 pound per cubic inch. This value is approximately 9 to 17 percent greater than the densities of the cobalt-base alloys with which the previous comparisons are made. The higher densities of these experimental alloys would naturally be reflected in any comparison with conventional cobalt-base alloys on the basis of strength to weight ratio. On this basis, these experimental alloys would still compare favorably with HS-31; however, such a comparison would result in somewhat lower values for the experimental alloys than the other conventional cobalt-base alloys shown in figures 3 and 4.

Tensile properties

The tensile properties of alloys Co-25W-1Ti-0.4C and Co-25W-1Ti-1Zr-0.4C are summarized in Table I. The alloys have good ductility, as indicated by the high elongations that range between approximately 14 and 22 percent for the

Catastrophic oxidation did not occur with either of these alloys in the unprotected condition even at the highest test temperatures. Life was extended slightly by a commercial aluminum-iron diffusion coating. It should be noted, however, that other coatings may provide superior protection; this aspect remains to be investigated.

Figure 6(a) compares the alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C at 1850° F and 15,000 psi with two commonly used cobalt-base alloys, HS-31 (ref. 10) and WI-52 (ref. 11), at 1800° F, the highest temperature for which data were available for the latter two alloys. It is evident that, even at a temperature 50° F higher, the alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C has better stress-rupture properties up to 1000-hour life. Figure 6(b) provides a similar comparison at 2000° F with two of the most recent conventional cobalt-base alloys. The 3-percent-Cr - 2-percent-Re modified alloy shows marked improvement over SM-302 (ref. 9). At times less than 90 hours, the alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C also had better stress-rupture properties than SM-322 (ref. 13); at longer times, the curves of the latter two alloys were nearly coincident. It is significant that, while comparing favorably in strength with conventional high-chromium cast alloys, even the strongest alloys of the present investigation were readily workable.

Again, it should be noted that the densities of the experimental alloys are somewhat higher (approx. 8 to 13 percent) than the conventional high-chromium cobalt-base alloys with which comparison is made in figure 6. These higher densities would be reflected in any comparison that might be made on the basis of strength to weight ratio. Even on this basis, however, these two experimental alloys compare favorably with all of the conventional cobalt-base sheet material. Also, the relatively high as-hot-rolled room-temperature tensile strengths, which are as high as 204,400 psi, are worth noting. These should be of interest in room-temperature applications where reasonably high-strength sheet is required. In addition, the elevated-temperature strength of these alloys is sufficiently high to warrant consideration of their use for elevated-temperature sheet applications.

LOW-CHROMIUM-CONTENT ALLOYS

In a later phase of this program, the strongest alloy previously developed, Co-25W-1Ti-1Zr-0.4C, was modified by systematic additions of chromium and rhenium. Chromium was considered because it had been shown to be one of the most effective elements for strengthening the binary alloy Co-25W (ref. 8). Rhenium was considered as a potential solid-solution strengthener. Both elements were held to low levels, chromium because of its volatility and rhenium because of its cost.

The two strongest alloys were Co-25W-1Ti-1Zr-3Cr-0.4C and Co-25W-1Ti-1Zr-3Cr-2Re-0.4C. Again, chemistry generally corresponds to these designations except for zirconium (see ref. 2). The theoretical densities of these alloys are 0.359 and 0.363 pound per cubic inch, respectively.

Stress rupture properties

Figure 5 illustrates the as-cast stress-rupture properties of alloys Co-25W-1Ti-1Zr-3Cr-0.4C (fig. 5(a)) and Co-25W-1Ti-1Zr-3Cr-2Re-0.4C (fig. 5(b)) at several temperatures. Lines (best visual fit) are drawn through the average-life values obtained at each stress level with uncoated test specimens. It is significant that both alloys have long life over a wide range of stresses at temperatures up to 2000° F. In the uncoated condition at 2200° F, the chromium-rhenium modified alloy had a rupture life of 23 hours at a stress of 5000 psi.

alloys in figure 6, except SM-322, over a wide portion of the life range considered.

Tensile properties

The tensile properties of the alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C are shown in figure 7. The average as-cast room-temperature tensile strength was 98,050 psi, and the average elongation was 2.3 percent. At 1800° F, the as-cast tensile strength was almost 40,000 psi, and the average elongation increased substantially to 26.2 percent. The high elevated-temperature ductility undoubtedly accounts for the ease with which these alloys were hot-rolled.

The tensile strength of sheet in the annealed condition (1/2 hr at 2350° F and water quenched) is virtually identical to the as-cast tensile strength from 1600° to 1800° F. At room temperature, the sheet had an average tensile strength of 181,750 psi, almost twice as high as the as-cast value.

Increases in room-temperature ductility of approximately one order of magnitude over the as-cast condition were observed with the sheet material. At 1600° F, the ductility of the sheet was appreciably less than at room temperature, yet greater than that of the cast material. At 1800° F, the elongation of the sheet material was approximately 35 percent.

WORKABILITY

Since good workability is another major requirement for advanced power-system ducting and radiator applications, attempts were made to roll both the chromium-free and the low-chromium alloys. Chill-cast slabs generally 2 by 2 by 1/2 inch thick were hot-rolled at 2150° F to 0.060-inch-thick sheet, and no edge cracking was observed. Sheet of the low-chromium alloys was further reduced to a thickness of 0.013 inch by cold-rolling with intermediate anneals.

The ease with which these alloys can be rolled suggests that they can be formed into the complex shapes required for radiator and ducting components of advanced space-power systems, as well as other high-temperature aerospace applications.

OXIDATION RESISTANCE

Figure 8 shows the oxidation behavior at 1900° F of several alloys in this series compared with unalloyed cobalt and with WI-52, a cast cobalt-base alloy that contains 21 percent chromium. The data are presented on the basis of weight gain per unit initial area. The alloys that contain 3 percent chromium together with 1 and 3 percent rhenium show a slightly better oxidation resistance than the alloys containing no chromium and considerably better oxidation resistance than unalloyed cobalt. The alloy WI-52 has substantially greater resistance to oxidation than the alloys containing only 3 percent chromium, as might be expected. The 3-percent-Cr - 2-percent-Re modified alloy was also tested in the coated condition. The weight gain observed was negligible. The commercial aluminum-iron diffusion coating employed offered excellent protection for unstressed specimens. The coating, however, appears to have only limited ductility. When used on highly stressed specimens that elongated appreciably during stress-rupture testing, it was effective in preventing oxidation. Once the substrate had elongated and the coating had cracked, oxidation was not inhibited.

POTENTIAL APPLICATIONS

Although much additional work must be done in order to understand the behavior of these alloys, the data obtained indicate that they have considerable potential. In addition to the originally intended application to space power systems, where oxidation is not a primary concern, these alloys should be applicable in other areas as well. For example, their potentially lower evaporation rate in vacuum suggests that they may be used in industrial vacuum furnaces where high-temperature strength and low volatility are required. Another important area of application is in turbojet-engine components. The combination of excellent formability together with high-temperature strength suggests advantageous uses in such jet-engine components as combustion chambers, tailpipe assemblies, and stator vanes. Since advanced jet-engine designs now call for coating protection on many such high-temperature components, the relatively lower oxidation resistance of these alloys compared with high-chromium cobalt-base alloys need not preclude their use in these areas.

The possibility of applying these alloys to turbojet engines is further pointed up by the work being done at the Union Carbide Stellite Corporation. It is reported (ref. 14) that the alloy Co-25W-1Ti-0.5Zr-0.4C, referred to as "Haynes" Developmental Alloy No. 8168, has excellent strength characteristics. After using conventional investment-casting procedures and utilizing vacuum melting and remelting, test parts were diffusion-coated to improve oxidation resistance. As-coated with the Haynes C-12 diffusion coating, the alloy had a 365-hour life and 23-percent elongation at 2000° F and a stress of 10,000 psi. Tests at 2100° F show the alloy to have excellent resistance to thermal shock. The "bow" observed during thermal-shock testing showed the alloy to compare favorably with current production vane alloys. No cracking of this alloy occurred in any of the tests. It is indicated that the alloy would probably be a satisfactory vane material for advanced engine designs (ref. 14).

The low-chromium alloys in this series might be expected to have an even greater potential for turbine-engine-vane applications in view of their higher elevated-temperature strength and equally good rollability. Work is also being done in industry with at least one of these alloys. The Florida Research and Development Center of Pratt and Whitney Aircraft has recently embarked on a program with the Stellite Division of the Union Carbide Corporation to evaluate the effects of processing on the performance of the Co-25W-1Ti-1Zr-3Cr-2Re-0.4C alloy.

CONCLUDING REMARKS

In view of the potential of cobalt-refractory-metal superalloys for high-temperature aerospace applications, research is continuing at the NASA with these alloys in order to further delineate their properties. Although these alloys were developed for space-power-system applications, their advantageous properties suggest that they be considered for other high-temperature aeronautical and industrial applications as well.

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12. Haynes Data Folder, June 1962.

13. SM-322 - High Temperature Cobalt Base Superalloy. Martin Metals Co., 250 North 12th St., Wheeling, Illinois.

14. Preliminary Data, "Haynes" Developmental Alloy No. 8168, Feb. 14, 1964.

TABLE I. - TENSILE PROPERTIES OF ALLOYS Co-25W-1Ti-0.4C AND Co-25W-1Ti-1Zr-0.4C

Alloy	Condition	Test temperature, °F	Ultimate tensile strength, psi	Elongation, percent
Cast				
Co-25W-1Ti-0.4C	As-cast	Room	97,000	6.2
	As-cast	1800	44,870	12.5
Co-25W-1Ti-1Zr-0.4C	As-cast	Room	98,580	3.5
Sheet				
Co-25W-1Ti-0.4C	As-rolled	Room	204,400	22.6
	Solution treated at 2475° F	Room	106,000	14.4
	Solution treated at 2400° F	Room	144,250	20.3
	Solution treated at 2400° F	1800	34,800	15.5
Co-25W-1Ti-1Zr-0.4C	As-rolled	Room	179,300	20.2
	Solution treated at 2400° F	Room	147,030	20.5
	Solution treated at 2400° F	1800	38,250	19.5

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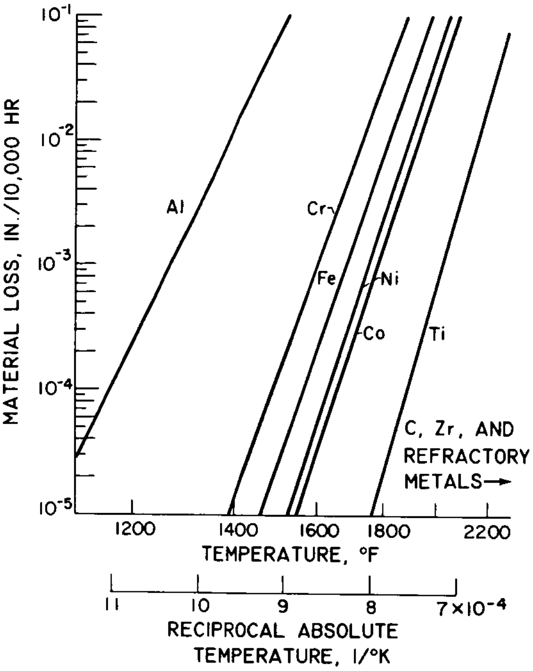

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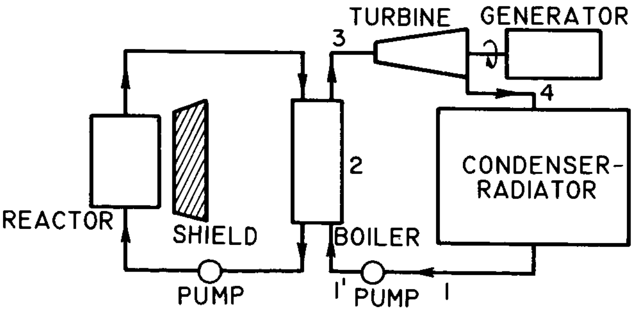
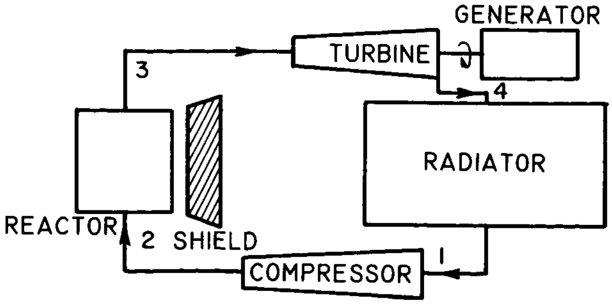
Figure 1. - Material loss in vacuum as function of temperature for several metals (ref. 3).



(a) RANKINE (VAPOR) CYCLE



(b) BRAYTON (GAS) CYCLE

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Figure 2. - Nuclear turbogenerator cycles (ref. 5).

E-2906

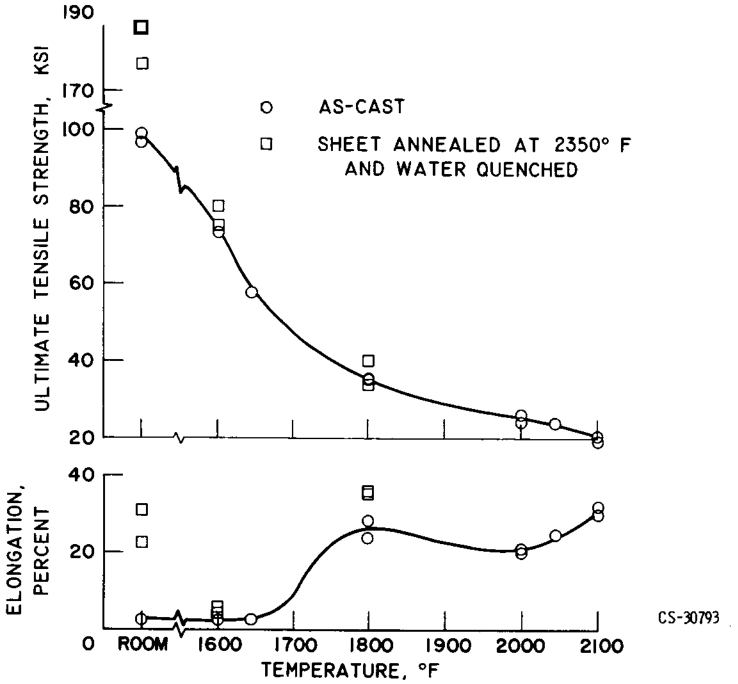

Figure 7. - Tensile properties of Co-25W-1Ti-1Zr-3Cr-2Re-0.4C as function of temperature.

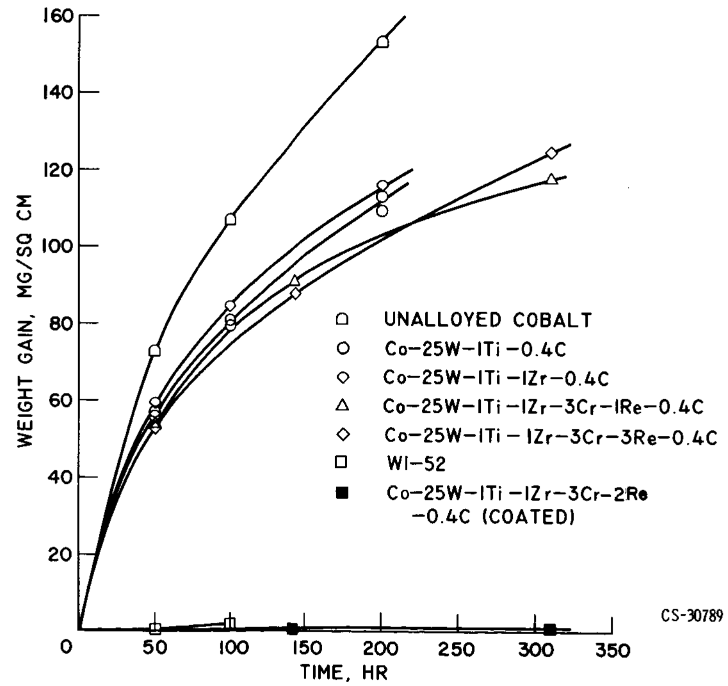

Figure 8. - Weight gain per unit area as function of time in air at 1900° F for unalloyed cobalt and several cobalt-base alloys.

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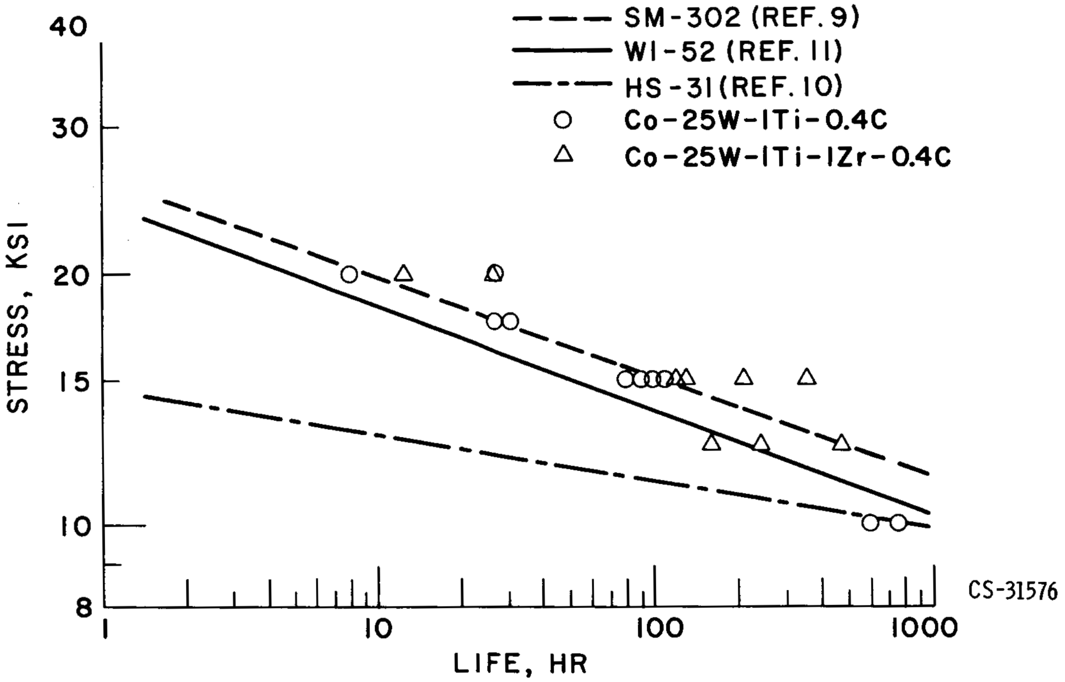


Figure 3. - Stress-rupture properties at 1800° F of several cast cobalt-base alloys in air.

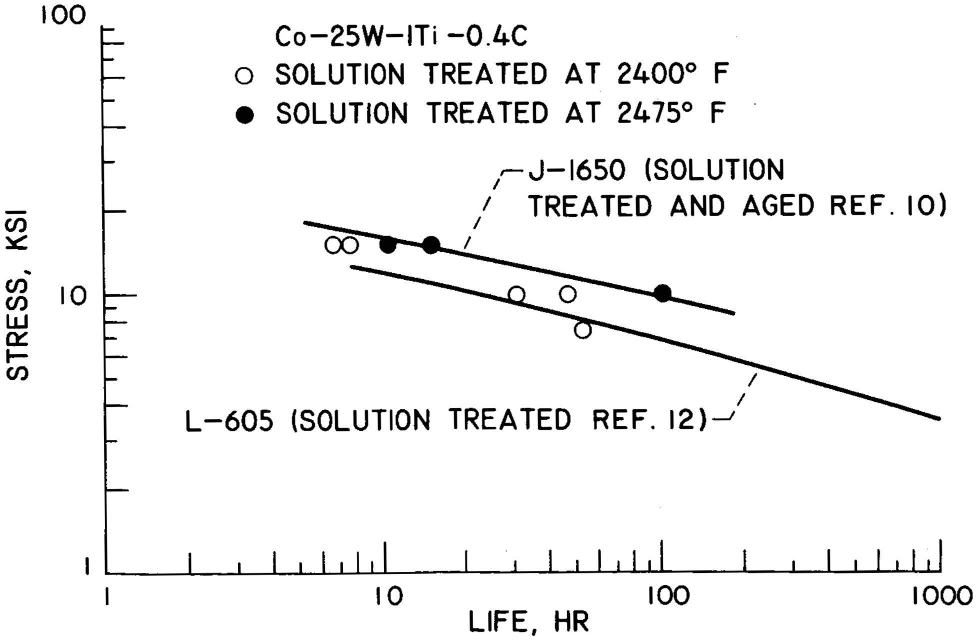
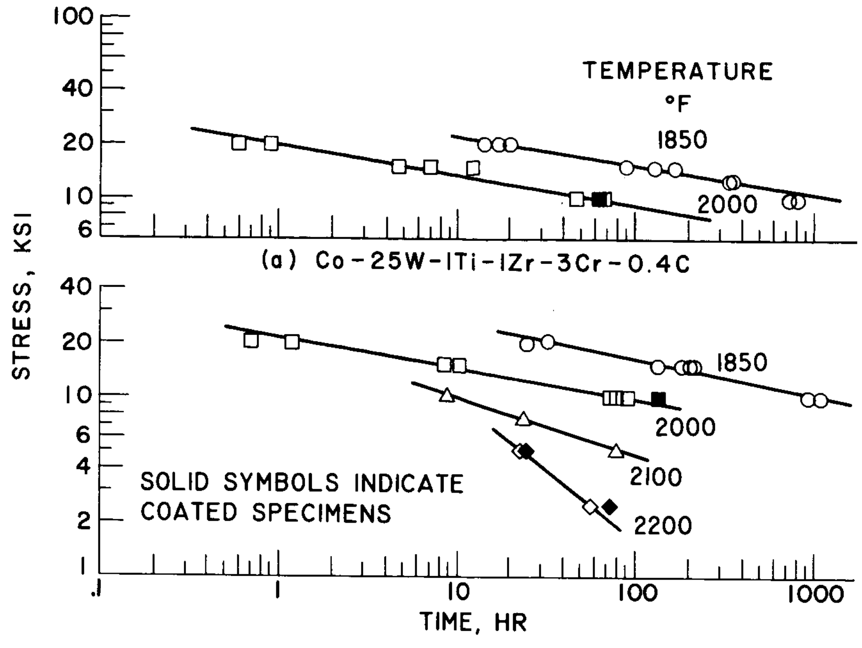


Figure 4. - Stress-rupture properties of Co-25W-1Ti-0.4C alloy sheet at 1800° F in helium compared to current cobalt-base sheet alloys.



(a) Co-25W-1Ti-1Zr-3Cr-0.4C

(b) Co-25W-1Ti-1Zr-3Cr-2Re-0.4C

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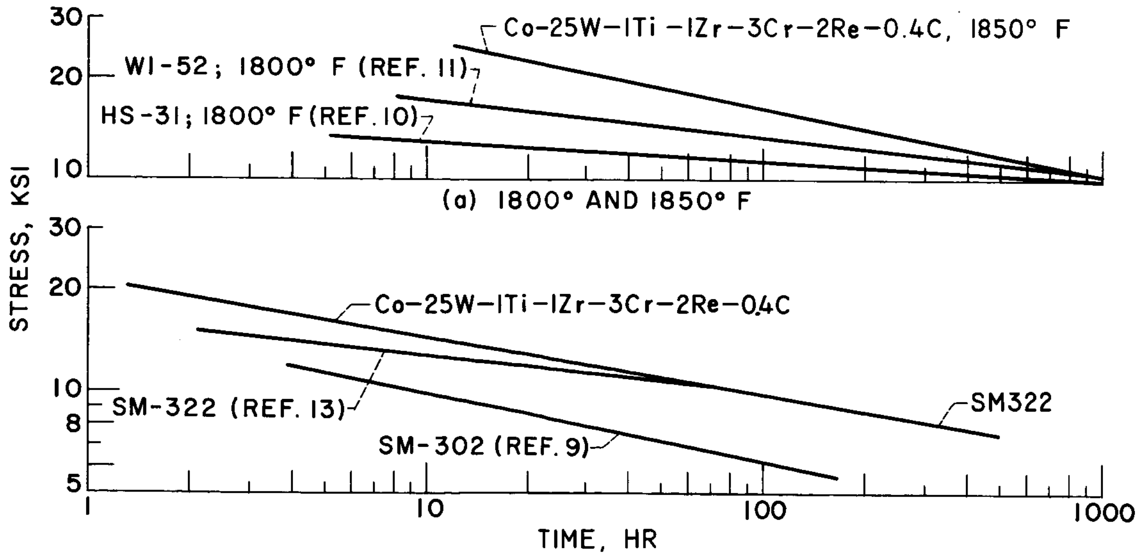
Figure 5. - Stress-rupture properties of chromium- and chromium-rhenium-modified cobalt-base alloys.



(a) 1800° AND 1850° F

(b) 2000° F

CS-30791

Figure 6. - Comparison of stress-rupture properties of alloy Co-25W-1Ti-1Zr-3Cr-2Re-0.4C with conventional cobalt-base alloys.