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ELEVATED-TEMPERATURE CREEP AND TENSILE PROPERTIES OF THREE COLUMBIUM-BASE ALLOYS

by

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ABSTRACT

In work to develop materials for elevated temperature applications, binary columbium alloys containing either 2.37 w/o chromium, 3.34 w/o zirconium, or 5.21 w/o vanadium were fabricated to sheet by forging at 550 C and rolling at room temperature. All three alloys were completely recrystallized after 90 per cent cold work (reduction in thickness) and a one hour anneal at 1150 C.

Tensile tests on the annealed materials at 650, 800, 1000, 1150, and 1315 C indicated that chromium, zirconium, and vanadium are potent strengtheners of columbium. At 1000 C the 2.37 w/o chromium and the 5.21 w/o vanadium alloys had 0.2 per cent offset yield strengths of 38,000 psi and 38,300 psi respectively. At 1315 C, the 3.34 w/o zirconium alloy had a 0.2 per cent offset yield strength of 14,700 psi.

Stresses to produce creep rates of 0.0001, 0.01, and 0.1 per cent per hour were determined for all three alloys at 650, 800, and 1000 C. The vanadium alloy exhibited the greatest creep resistance, requiring stresses of 52,700, 40,000, and 15,500 psi to produce a creep rate of 0.001 per cent per hour at 650, 800, and 1000 C respectively.

This research indicates that significant improvement in the mechanical properties of columbium can be achieved by alloying without undue sacrifice of fabricability.

FIGURE 1. EFFECT OF ANNEALING TEMPERATURE ON ROOM-TEMPERATURE HARDNESS OF COLUMBIUM-BASE ALLOYS

FIGURE 2. MICROSTRUCTURES OF COLUMBIUM-3.34 w/o ZIRCONIUM ALLOY AS COLD ROLLED AND AS ANNEALED

FIGURE 3. EFFECTS OF TEMPERATURE ON THE TENSILE STRENGTH OF COLUMBIUM-BASE ALLOYS AND UNALLOYED COLUMBIUM

FIGURE 4. STRESS VERSUS MINIMUM CREEP RATE FOR THREE COLUMBIUM-BASE ALLOYS AT 650, 800, AND 1000 C.

FIGURE 5. DESIGN CURVES FOR COLUMBIUM-2.37 w/o CHROMIUM ALLOY

FIGURE 6. DESIGN CURVE FOR COLUMBIUM-3.34 w/o ZIRCONIUM ALLOY

FIGURE 7. DESIGN CURVES FOR COLUMBIUM-5.21 w/o VANADIUM ALLOY

FIGURE 8. TEMPERATURE VERSUS STRESS TO RUPTURE AT 10, 100, AND 1000 HR FOR THREE COLUMBIUM-BASE ALLOYS

Elevated-Temperature Creep and Tensile Properties of Three Columbium-Base Alloys*

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The study of columbium-base alloys for elevated temperature applications is generally motivated by the desire to develop materials which have high resistance to creep while maintaining the excellent fabricability of unalloyed columbium. The alloying additions used in this investigation were selected to produce alloys which would have a maximum of mechanical strength and a minimum of difficulty in fabrication. Because of this the alloying additions were limited to those which would produce solid solution alloys. Therefore the increased strength is limited generally to that obtainable through solid-solution strengthening mechanisms. Initially binary and ternary alloys containing additions chromium, molybdenum, titanium, tantalum, vanadium, and zirconium were made [1,2]. These initial studies indicated that chromium, vanadium, and zirconium showed the most promise for additional studies. The nominal compositions selected were columbium-2 w/o chromium, niobium-3.5 w/o zirconium, and niobium-5.2 w/o vanadium.

The above mentioned alloys were prepared by consumable-electrode arc-melting techniques from high-purity melting stock. Analyses for the melting stock and alloying additions are shown in Tables 1 and 2. Zirconium additions were made in the form of sheet which was welded onto the 3/4-in. diameter columbium rod.

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* Work performed under AEC Contract W-7405-eng-92.

TABLE 1. CHEMICAL ANALYSES OF COLUMBIUM MELTING STOCK[(a)]

Impurity Element	Amount, ppm	Impurity Element	Amount, ppm
Aluminum	<20	Molybdenum	<20
Boron	<1	Nickel	<20
Cadmium	<5	Nitrogen	60-85
Carbon	30	Oxygen	85
Chromium	<20	Silicon	100-160
Copper	<40	Tin	<20
Hydrogen	<20	Tantalum	570-630
Iron	<100	Titanium	<150
Lead	<20	Tungsten	<300
Magnesium	<20	Vanadium	<20
Manganese	<20	Zinc	<20
		Zirconium	<500

(a) Analysis furnished by Wah Chang Corporation.

TABLE 2. CHEMICAL ANALYSES OF ALLOYING ADDITIONS FOR COLUMBIUM-BASE ALLOYS

Impurity	Analysis of Indicated Addition Element, ppm Chromium	Zirconium	Vanadium
Carbon	10	50	400
Hafnium	--	<200	--
Hydrogen	--	--	6
Iron	--	200	190
Nitrogen	--	60	280
Oxygen	15	--	830
Silicon	<20	--	--
Tin	<20	--	--
Vanadium	<3	--	--
Zirconium	<20	--	--

The chromium and vanadium additions were made in the form of granules which were welded into place in 1/4 deep grooves on the niobium rod. The chromium addition was overcharged approximately 50 per cent to compensate for losses due to vaporization during melting.

The electrodes thereby prepared were consumably arc melted (argon atmosphere) into a water-cooled copper crucible. After melting, the ingots were lathe turned top and bottom, quartered, rewelded into electrodes, and remelted. After the second melt the ingots were cropped and turned on a lathe to remove surface imperfections. The ingots weighed approximately 3 lbs after the above conditioning. Turnings from the top and bottom of each ingot were analyzed. The results of these analyses are shown in Table 3. The compositions were sufficiently close to that desired and impurity pickups during melting were minimial and considered to be acceptable for this study. Microstructural examination shows all three alloys to be clean single phase structures.

Ingots of each alloy were soaked for 30 min prior to forging at 550 C in a furnace through which helium constantly flowed. After soaking the alloy ingots were reduced approximately 50 per cent by forging. During forging care was taken to work the ingot slowly until surface deformation was noted; after the surface had been worked lightly, the ingot could be worked more heavily. The forged slabs were then "warm" (550 C) rolled to 0.200-in-thick sheet. This sheet was subsequently vapor blasted to remove a slight surface oxide and rolled to 0.040 in thick sheet at room temperature.

TABLE 3. RESULTS OF CHEMICAL ANALYSES OF AS-CAST INGOTS TOP AND BOTTOM

Alloy Composition (Balance Columbium), w/o		Impurity Content, ppm			
Nominal	Analyzed	Oxygen	Hydrogen	Nitrogen	Carbon
2.0 chromium	2.37 chromium	90	<2	--	--
3.0 zirconium	3.34 zirconium	118	<1	95	40
5.2 vanadium	5.21 vanadium	185	<2	--	--

The temperature at which recrystallization was complete was determined for all three alloys studied. The alloys were reduced 90 per cent (reduction in thickness) and given a 1 hr vacuum anneal which was followed by furnace cooling. Specimens were annealed over the temperature range from 980 through 1315 C at 55 C intervals.

After annealing Vickers hardness measurements were made on each specimen and the results obtained are shown plotted versus annealing temperature in Figure 1. It can be readily seen that both the columbium and the columbium alloys underwent a large decrease in hardness between room temperature and 980 C. The hardness of the columbium-2.37 w/o chromium and columbium-5.21 w/o vanadium alloys showed no change above this temperature to 1315 C, while the hardness of the columbium and columbium-3.34 w/o zirconium alloy continued to decrease up to 1095 C before a similar plateau was evident.

A set of typical microstructures of the columbium-3.34 w/o zirconium alloy in various stages of recrystallization is shown in Figure 2. Figure 2a shows the structure as cold worked. Annealing at 980 C (Figure 2b) produced no appreciable change. However, the structure of the specimen annealed at 1095 C (Figure 2c) shows a partially recrystallized structure while after annealing at 1150 C (Figure 2d) recrystallization was complete. Evidence of grain growth as a result of annealing at a still higher temperature (1200 C) is shown in Figure 2e. The 2.37 w/o chromium and 5.21 w/o vanadium alloys showed complete recrystallization after annealing at 1150 C.

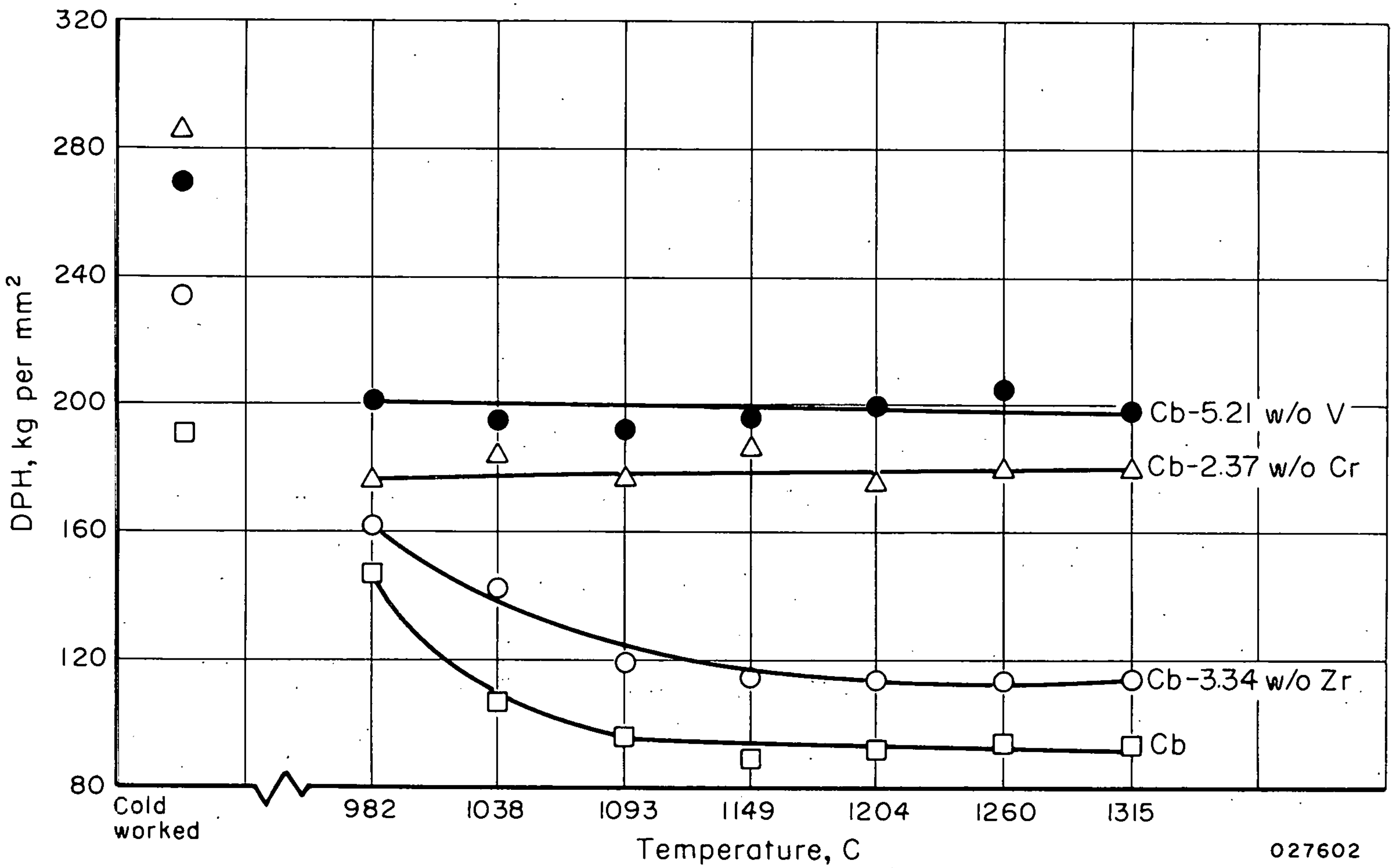
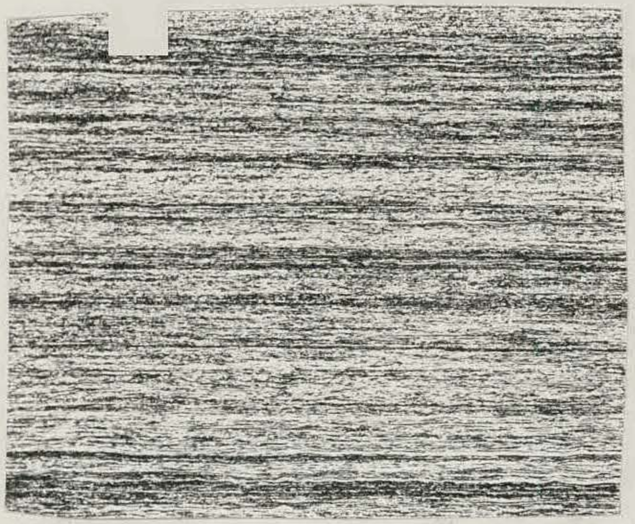


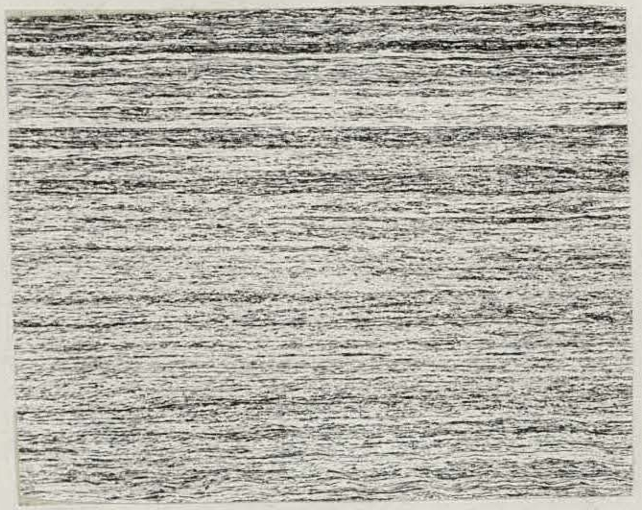
FIGURE 1. EFFECT OF ANNEALING TEMPERATURE ON ROOM TEMPERATURE HARDNESS OF COLUMBIUM-BASE ALLOYS



100X RM18362

a. Cold Rolled

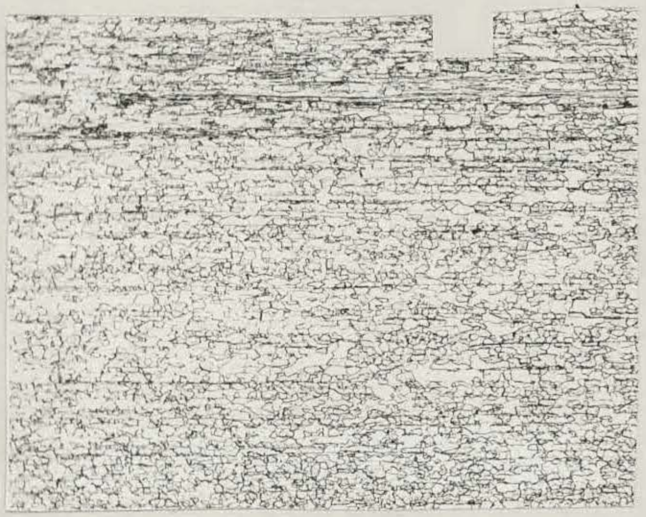
DPH is 236 (10-kg load). This structure was typical of all alloys studied.



100X RM18408

b. Annealed 1 Hr at 980 C

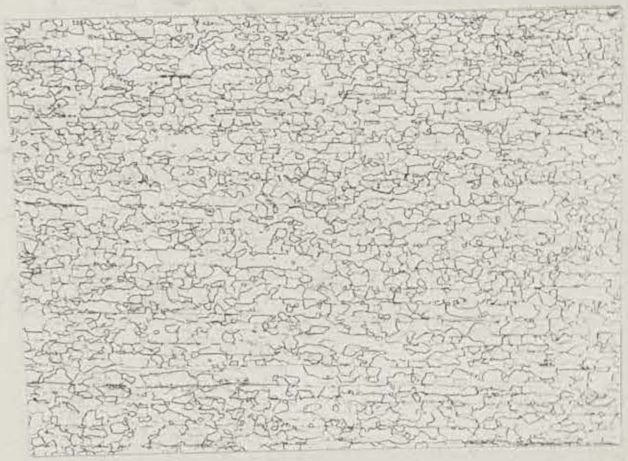
DPH is 163 (10-kg load).



100X RM18364

c. Annealed 1 Hr at 1095 C

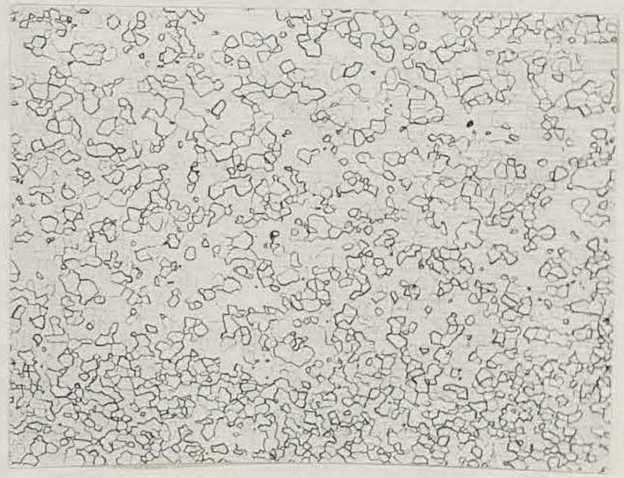
DPH is 120 (10-kg load). Recrystallization has started but is incomplete.



100X RM18165

d. Annealed 1 Hr at 1150 C

DPH is 114 (10-kg load). Recrystallization is complete.



100X RM18163

e. Annealed 1 Hr at 1205 C

DPH 115 (10-kg load). Recrystallization is complete and grain growth has started.

FIGURE 2. MICROSTRUCTURES OF COLUMBIUM-3.34 W/O ZIRCONIUM ALLOY AS COLD ROLLED AND AS ANNEALED

Because recovery occurs below the recrystallization temperature, no pronounced drop in hardness occurs at the temperature at which recrystallization is observed. It took approximately 1 hr to heat the specimens to the selected annealing temperature during which time stress relief and reduction in strain energy apparently eliminated all but a limited number of strain centers having sufficient energy to initiate the growth of new grains. Thus the microstructures achieved above the recrystallization temperature represent the product both of recrystallization in areas where such strain centers were available and of simple grain growth, when the strain energy was insufficient to nucleate new grains. The grains undergoing grain growth maintained their cold-worked alignment to yield the final microstructure observed. Equiaxed, recrystallized grains are interspersed between these slightly aligned grains.

Tensile tests were performed at 650, 800, 1000, 1150, and 1315 C on sheet specimens parallel to the direction of rolling. A strain rate of 0.002 in. per in. per min in the elastic region was maintained. The strain rate was increased to 0.013 in. per in. per min beyond the proportional limit. All tests were performed in a vacuum of less than 1×10^{-3} mm of mercury. The effect of temperature on the tensile properties of the columbium alloys investigated are shown in Figure 3. On a weight per cent basis chromium appears to be the most potent strengthener of columbium up to 1150 C, although the properties of the chromium and of the vanadium alloy are about equal.

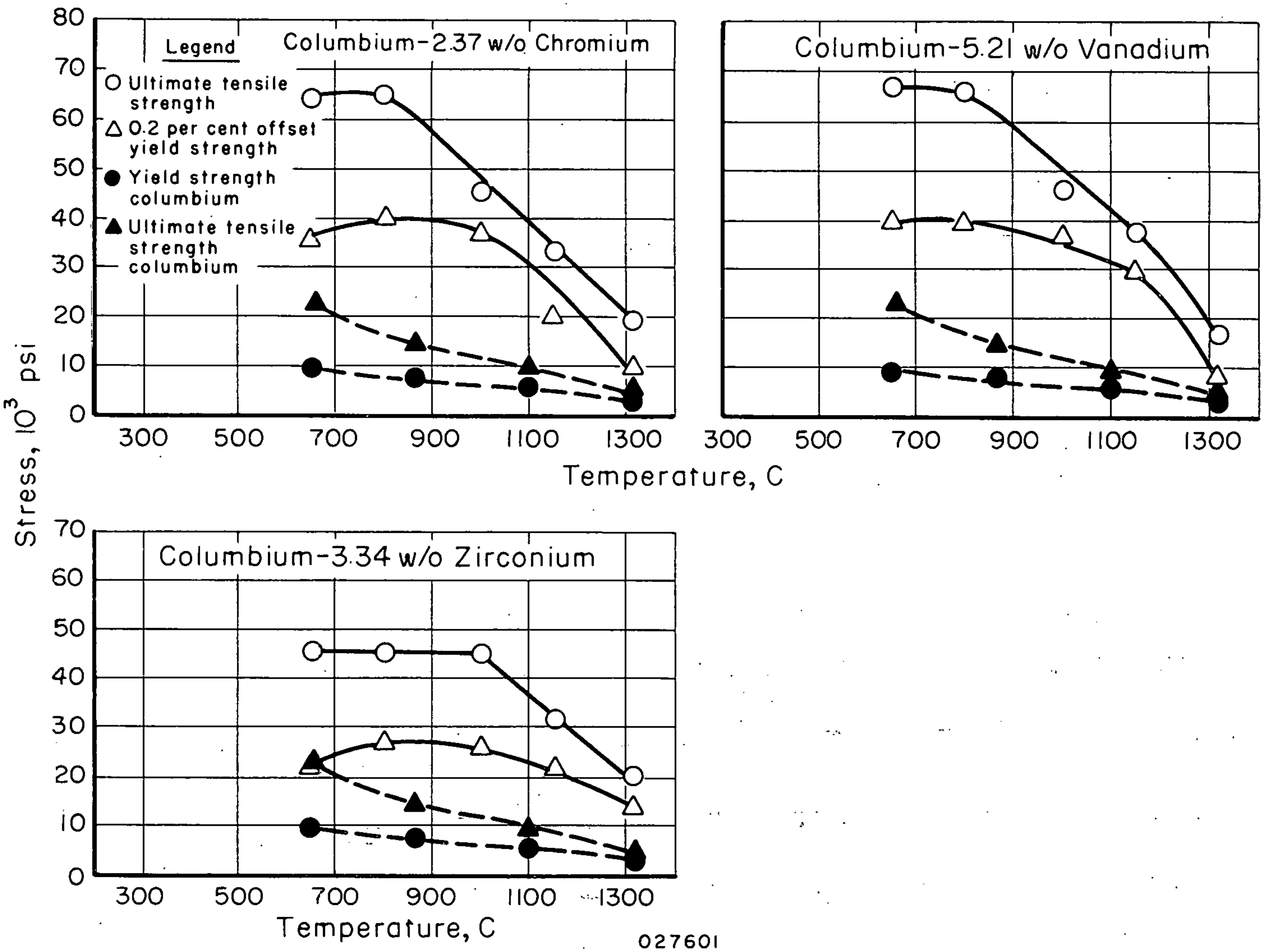


FIGURE 3. EFFECTS OF TEMPERATURE ON THE TENSILE STRENGTH OF COLUMBIUM-BASE ALLOYS AND UNALLOYED COLUMBIUM

All of the specimens were annealed 1 hr at 1450 C prior to testing.

A summary of the stresses that will produce creep rates of 0.001, 0.01, and 0.1 per cent per hr at 650, 800, and 1000 C is shown in Table 4. The creep rates obtained from all tests are plotted in Figure 4. Stresses producing the selected creep rates shown in Table 4 were taken from this graph.

Most of the test specimens behaved in a normal manner; however, the columbium-3.34 w/o zirconium alloy showed some unusual characteristics at 650 and 800 C. The specimens at 650 C were loaded to very high stresses since previous work with an alloy of similar composition had shown that at this temperature no creep was observed until the ultimate strength was approached. At 650 C, the alloy either failed on loading or continued on test indefinitely at a very low creep rate. The difference in stress for failure on loading and for essentially continuous service is very small and essentially the same stress could produce either. In the case of the short-time failures, the load applied was either equal to or above the ultimate tensile strength of the alloys, which would be expected to result in failure. In the specimens which did not fail during testing, large (6 to 10%) initial elongations were noted. Also, at 650 C, the strain hardening introduced by the initial deformation in the zirconium alloy was apparently sufficient to produce appreciable strengthening. Since the test temperature of 650 C is about 500 C below the recrystallization temperature for this alloy, recovery is slow, and, the alloy is not rate sensitive so that practically no difference in the stresses is required to produce creep rates of 0.001, 0.01, and 0.1 per cent per hr.

TABLE 4. STRESSES TO PRODUCE CREEP RATES OF 0.001, 0.01, AND 0.1 PER CENT PER HR IN THREE COLUMBIUM-BASE ALLOYS

Alloy Composition (Balance Columbium), w/o	Stress, psi, to Produce Creep Rate Shown		
	0.001 Per Cent per Hr	0.01 Per Cent per Hr	0.1 Per Cent per Hr
		At 650 C	
2.37 chromium	47,800	53,200	58,700
3.34 zirconium	41,400	41,800	42,300
5.21 vanadium	52,700	58,800	64,700
		At 800 C	
2.37 chromium	35,000	37,800	40,600
3.34 zirconium	31,300	40,200	42,200
5.21 vanadium	40,000	42,500	45,000
		At 1000 C	
2.37 chromium	10,800	17,000	23,200
3.34 zirconium	9,000	15,300	20,800
5.21 vanadium	15,500	20,300	25,000

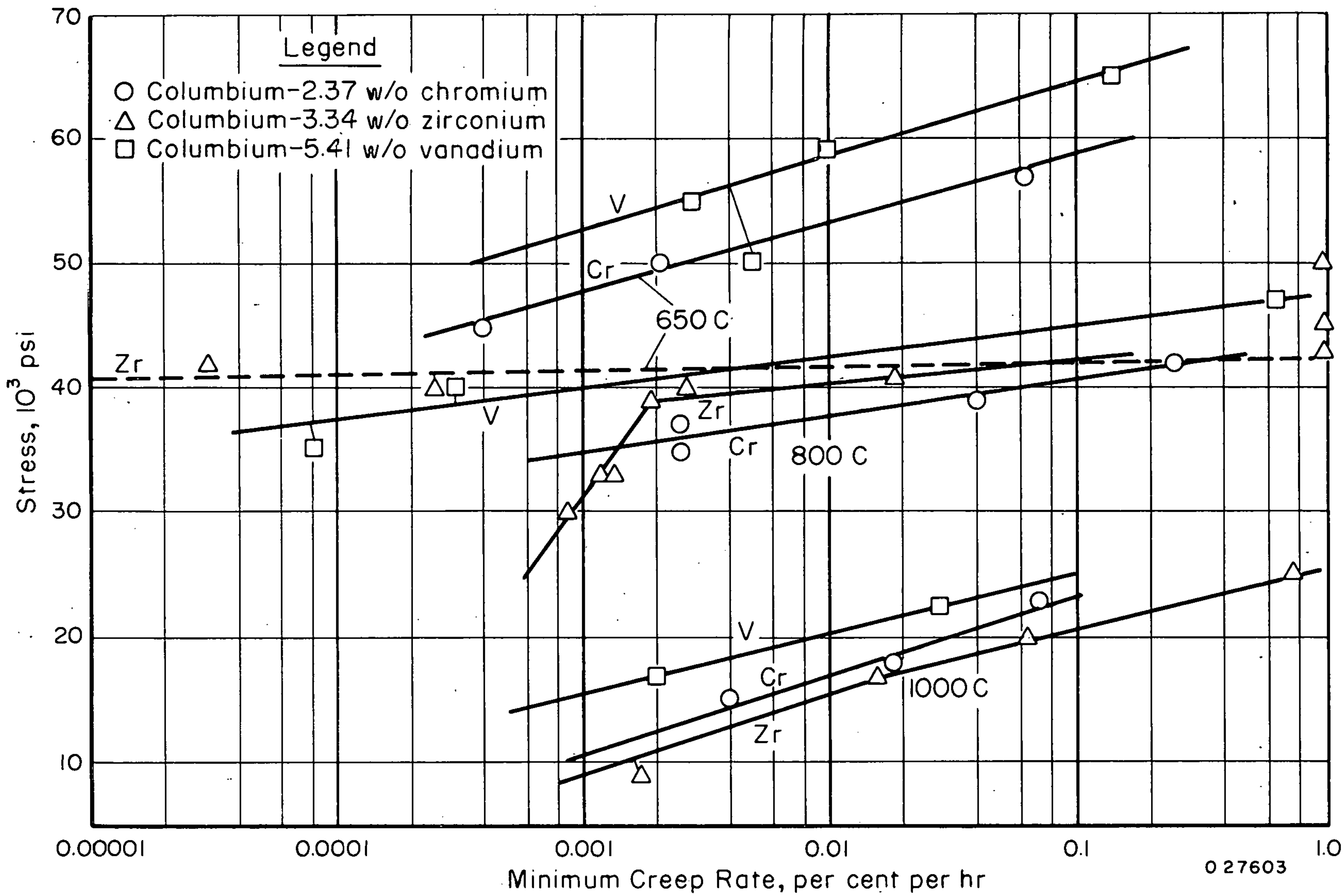


FIGURE 4. STRESS VERSUS MINIMUM CREEP RATE FOR THREE COLUMBIUM-BASE ALLOYS AT 650, 800, AND 1000 C

At 800 C, the stress-versus-minimum creep rate curve (Figure 4) for this zirconium alloy shows an abrupt change at about the stress required for a creep rate of 0.001 per cent per hr. This abrupt change is also probably a result of strain hardening, with the initial deformation introduced during the tests at the two higher stresses probably introducing enough strengthening to affect the creep properties. The transition noted in the stress-versus-creep rate curve for this alloy at 800 C very likely reflects differences in creep of slightly strained niobium-zirconium alloys and fully annealed materials.

At 1000 C strain-hardening effects were not noted, and normal creep behavior was observed for the zirconium alloy.

Design curves for each of the three alloys were prepared from creep test data and are shown in Figures 5, 6, and 7. These figures show rupture curves and also curves representing various percentages of total deformation as related to specific stresses and times. These deformations were not the same for each condition because identical deformations were not always available. Design curves were not prepared for the columbium 3.34 w/o zirconium alloy at 650 C because the necessary data were not available.

Stress-rupture data have been reproduced as curves of stress to rupture versus temperature in Figure 8. Data are shown for 10, 100, and 1000 hr to rupture for each alloy at each temperature. These curves represent the maximum stresses that the three alloys would tolerate under a particular stress-time-temperature situation.

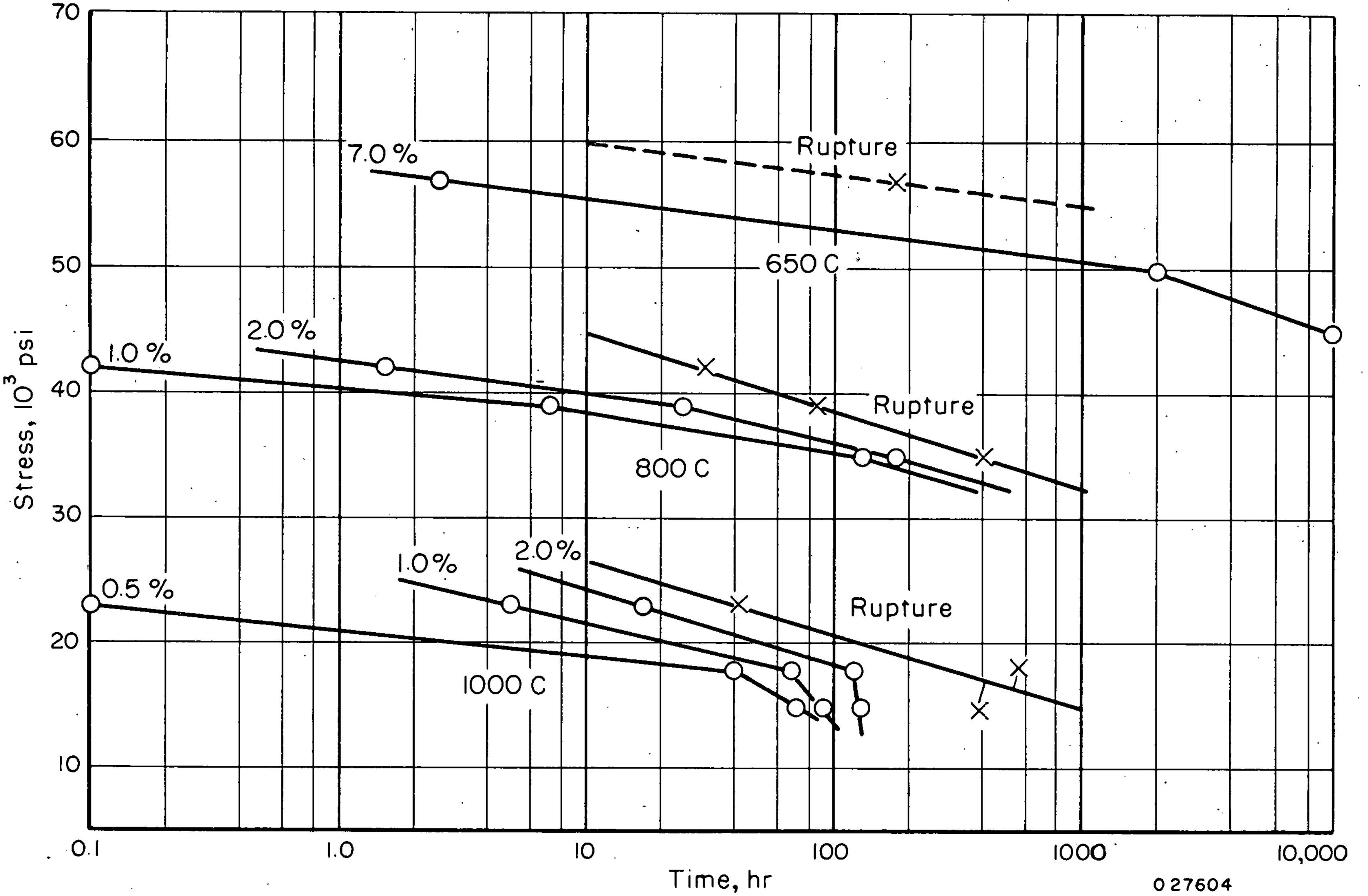


FIGURE 5. DESIGN CURVES FOR COLUMBIUM-2.37 w/o CHROMIUM ALLOY

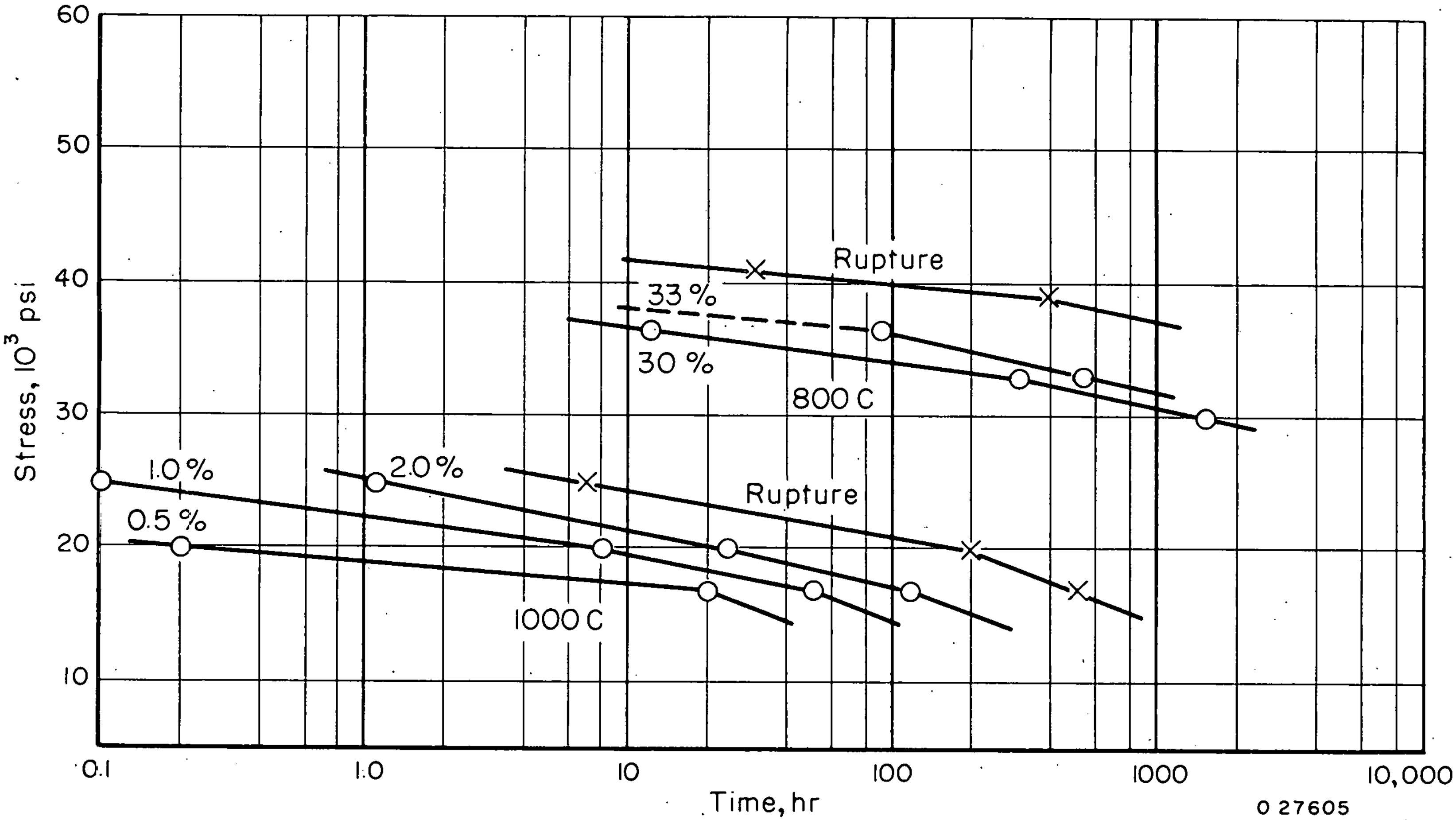


FIGURE 6. DESIGN CURVE FOR COLUMBIUM-3.34 w/o ZIRCONIUM ALLOY

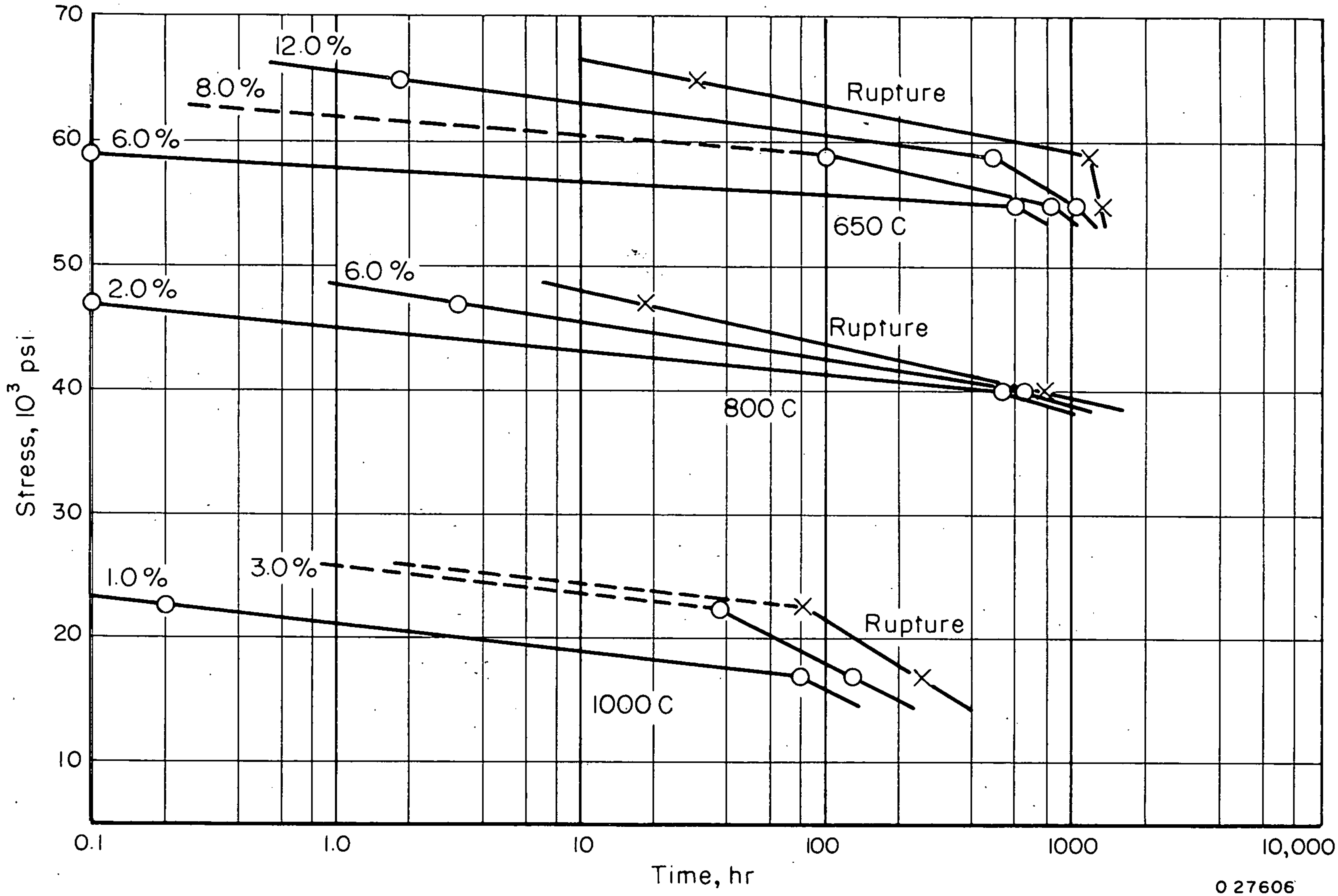


FIGURE 7. DESIGN CURVES FOR COLUMBIUM-5.21 w/o VANADIUM ALLOY

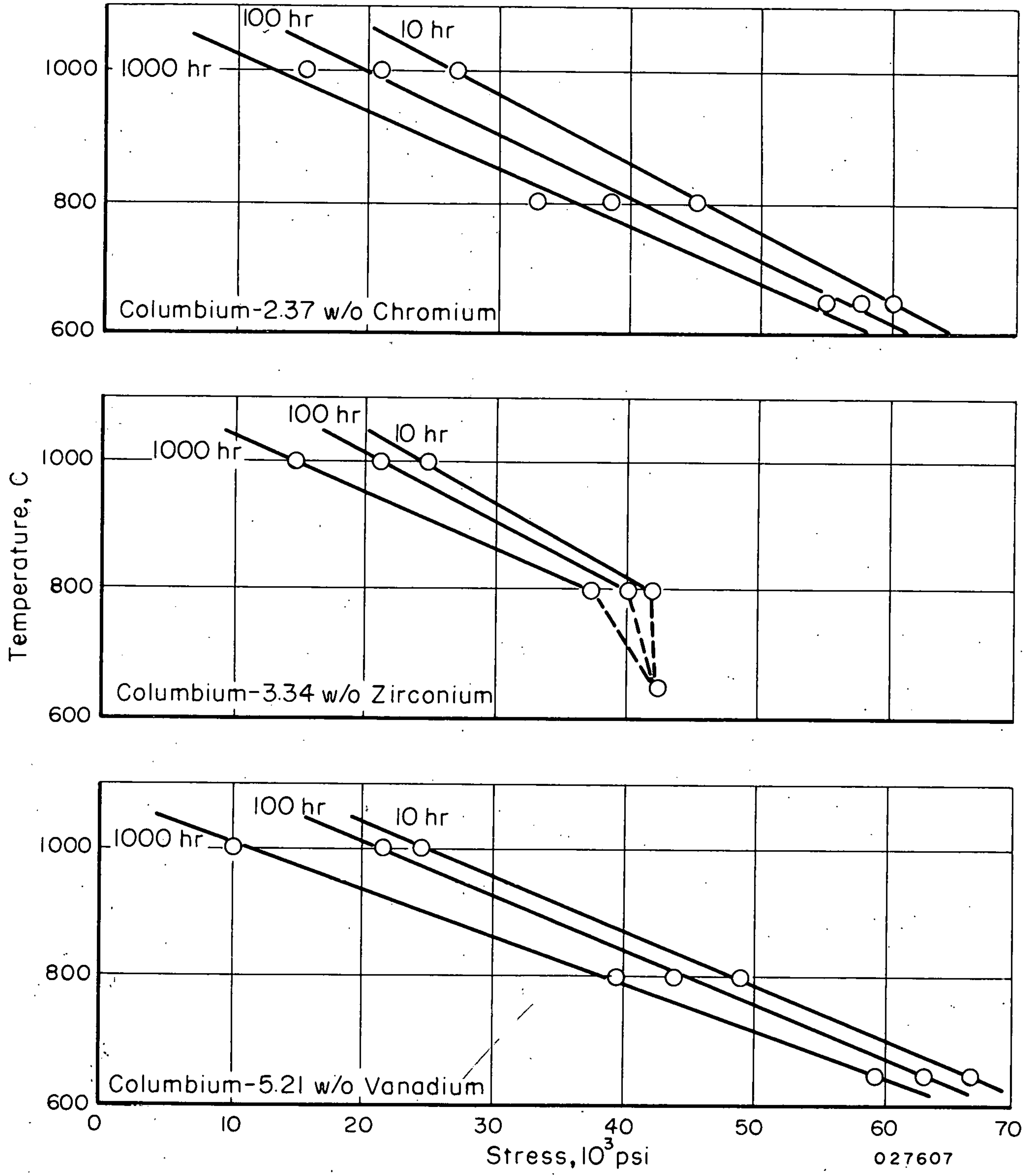


FIGURE 8. TEMPERATURE VERSUS STRESS TO RUPTURE AT 10, 100, AND 1000 HR FOR THREE COLUMBIUM-BASE ALLOYS

A careful analysis of the data presented indicates that the columbium-2.37 w/o chromium and columbium-5.21 w/o vanadium alloys are quite similar in creep properties, with the vanadium alloy having slightly better creep strength. The creep strength of the columbium-3.34 w/o zirconium alloy is generally poorer than the columbium-chromium or columbium-vanadium alloy.

As a result of the research discussed in the previous sections, it can be concluded that significant improvement in the mechanical properties of columbium can be achieved by alloying without undue sacrifice of fabricability. While ease of fabricability is impaired by alloying, alloys have been developed which should be amenable to fabrication by normal procedures.

REFERENCES

(1) DeMastry, J. A., Shober, F. R., and Dickerson, R. F., "Development of High Strength Niobium Alloys for Elevated Temperature Applications", BMI-1417 (February 22, 1960).

(2) DeMastry, J. A., Shober, F. R., and Dickerson, R. F., "High-Temperature Niobium-Base Alloys for Sodium-Cooled Reactors", BMI-1513 (April 14, 1961).