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AN IMPROVED TECHNIQUE FOR PRODUCING
HIGH SURFACE FINISH BERYLLIUM FOIL

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AN IMPROVED TECHNIQUE FOR PRODUCING HIGH SURFACE FINISH BERYLLIUM FOIL

John G. Avery and James F. Norris

Abstract. A method of producing beryllium foil with a better surface finish than present foil, and at a lower cost than the present method, has been conceptually developed. This method is performed with the rolls and the beryllium at 800°F, which is just below the temperature at which significant oxidation of beryllium begins. Subsequent annealing at 1200°F in a 10^{-6} torr vacuum produces a ductile foil whose surface does not require etching to remove oxide.

CONCLUSIONS

Based on the initial and final experimental work the following conclusions can be drawn.

- High quality surface finish beryllium foil can probably be produced on a four-high mill utilizing high hardness-high surface finish rolls which are heated to 800°F. High purity foil heated to 800°F would be rolled through the heated rolls inducing at least 50% total reduction. Annealing would be done at 1200°F for 3 hours at 10^{-6} torr level of vacuum.
- The above procedure is a reasonable extrapolation of experimental results; however, equipment does not exist at Rocky Flats to provide foil in this manner on a cast sales or production basis.
- If maximum ductility foil is desired, an anneal at a higher temperature than 1200°F is required, and subsequent etching is necessary to remove oxide.

In this method a cost savings of over 50% in process and labor costs can be realized as compared with the present cold roll method. This savings is possible because over half of the roll-anneal-etch stages in the conventional cold roll schedule (see Appendix I) can be eliminated by using heated rolls.

INTRODUCTION

Beryllium foil must be ductile and have uniform thickness so it can be fabricated into desired shapes. A high level of surface finish is also a desirable feature.

The present method of producing beryllium foil is long and tedious. The procedure (see Appendix I) involves a

number of stages in the three step rolling, annealing, and etching procedure which is required to produce a thin beryllium foil.

The present method of producing beryllium foil results in a low level of surface finish. After a particular amount of rolling, the foil is annealed to induce softness before rolling continues. An oxide layer is formed during this annealing. If the oxide layer is not removed before rolling is resumed, the oxide breaks up and, being harder than the beryllium, it becomes impregnated in the surface and causes a poor surface finish. To avoid this situation, the oxide is removed by a chemical etch after each annealing. This etching leaves an oxide free surface, but the as-rolled surface roughness increases from 15 rms to between 30 and 70 rms, depending on the etch used.

Another problem is the amount of labor involved in the present process. In addition to the time involved, as much as 20% of the foil is lost in each step of processing because of trimming of cracked portions of the foil. Therefore, from an economic standpoint it would be desirable to decrease the number of operations involved in producing the finished product.

Other metal foils are produced by rolling at low temperature so that oxidation is not a problem. High surface finish rolls produce a correspondingly high level of surface finish on the foil (usually less than 10 rms). The foil is then annealed in a protective atmosphere, or vacuum, at a temperature low enough to prevent oxide formation but adequate to provide a sufficient level of ductility in the finished foil.

The object of this investigation was to determine if a procedure similar to that used on more ductile metal foils could be developed for beryllium and produce a higher surface finish foil; preferably, at a lower cost than the present method. The improvements described are the results of several attempts at success in three areas of foil technology, namely; rolling, annealing, and etching. The initial work, which defined the basic limitations in the methods used to improve the foil production process, is described in the Initial Investigation section. The results of this initial investigation led to the technique described in the experimental procedure section.

INITIAL INVESTIGATION

Beryllium foil used in this investigation was produced by induction melting SR* grade flake into a billet 2 in. by 2 in. by 4-in. high. High purity foil is better from a fabrication standpoint, as it does not oxidize as severely during annealing as foil made from normal Rocky Flats purity level beryllium. High purity foil also produces better x-ray windows as it has a more uniform Z cross section. The billet was sectioned horizontally into sections, each 2 in. by 2 in. by 1-in. high. These were canned in stainless steel, the cans were electron beam welded, and rolled. After the beryllium was reduced from 1 in. to 0.080 in., the cans were removed and the beryllium sheet was reduced by bare rolling to 0.012-in. thickness. It was then annealed at 760°C and etched in a solution consisting of 48 vol% HNO₃-4 vol% HF-48 vol% H₂O to remove the surface oxide. The final sheet was 0.010-in. thick and had a surface finish of 70 to 90 in/in rms. The chemical composition of the billet is shown in Table 1.

Table 1. Chemical Composition of Induction Melted and Cast Ingots Made from SR Grade Flake.

Element	PPM	Element	PPM
B	13	Ti	1
O	50	Cr	10
Na	10	Mn	28
Mg	20	Fe	200
Al	10	Ni	10
Si	120	Ce	35
Cl	150	Pb	10
Ca	160	Ba	1

Foil Rolling

Rolling was done to determine if beryllium sheet could be cold rolled in high surface finish rolls as described in the introduction. A Stanat 6-in. mill was used for all rolling. A four-high setup was used, with 0.820-in.-diameter tungsten carbide work rolls and 6-in.-diameter backup rolls.** Roll speed was constant at 50 fpm for all rolling. The malleability of the foil was determined in the following manner: The mill setting was reduced 0.001 in. per pass. The foil was unidirectionally rolled. The appearance of heavy edge cracking or cracking away from the edges of the foil was taken to be indicative that the maximum reduction the foil could tolerate has been reached.† This

*SR is an electrolytically refined beryllium with lower impurity levels than commercially pure grades.

**Erroneous malleability values will result if the ratio of roll diameter to initial foil thickness is allowed to vary.

†Slight edge cracks, as the result of edge defects, were not counted as indicative of the maximum ductility until the cracks propagated well into the width of the sample.

maximum reduction will be referred to, in this report, as the total available ductility in the foil.

Room temperature (RT) rolling (that is, foil and rolls at RT) resulted in a total available ductility in the foil of 7%. This amount of reduction was insufficient to produce a 15 in/in surface finish, although it did improve the surface finish from 70 μ in/in to 40 μ in/in.

To increase the total available ductility the foil was heated before rolling. The available ductilities were determined for foil heated to 200, 400, 600, 800, and 1000°F, rolling through RT cold rolls. The results are shown in Figure 1. The graph also shows that total available ductility increases up to a value of 22% at 800°F. Above 800°F significant oxidation results and a grey surface layer forms. Therefore, 800°F is the maximum temperature for rolling to a bright, oxide-free surface.

In addition to determining the total available ductility as a function of foil temperature, the surface finishes were determined as a function of total reduction and foil temperature.

Figure 2 shows the percentage of the total available ductility needed to produce a given surface finish of 15 rms at various foil temperatures. As shown in Figure 2, at 200°F, 80% of the total available ductility is required to produce the same finish. The desirability of using only part of the available ductility to produce a quality foil became evident when various pieces of rolled foil were examined metallographically.

Referring to Figure 1, a number of combinations of foil temperature and reduction could be used to roll foil just short of the total available ductility point; 375°F and 13% were arbitrarily chosen.

Figures 3, 4, 5, and 6 show the starting sheet prior to room temperature rolling. There is an equiaxed structure with no microcracks.

This sheet was rolled 13% at 375°F which is just below the total ductility available as shown in Figure 1. Figures 7, 8, 9, and 10 show the as-rolled foil. The structural characteristics have been altered by the rolling operation. Low angle grain boundaries and microcracks are present. These microcracks are located in the interior of the foil. They will not weld or close during annealing and they are permanent and detrimental to the mechanical properties and uniformity of the foil. Further metallographic examination showed that, as the sheet was reduced, microcracking occurred slightly before macrocracking. Therefore, to produce internally sound foil it could only be reduced approximately 80% of the values given in Figure 1.

Figure 1. Total Available Ductility of 0.010-in. Beryllium Foil as a Function of Foil Temperature.

Figure 2. Percent of the Ductility-to-Fracture Needed to Obtain a 15 rms Finish as a Function of Foil Temperature.

Figure 3. Starting Sheet for Beryllium Foil Rolling Experiments Showing No Microcracks. Transverse view 200X. Bright Field.

Figure 4. Starting Sheet for Beryllium Foil Rolling Experiments Showing Equiax Structure. Transverse view 200X, Polarized Light.

Figure 5. Same Material as Shown in Figures 3 and 4. Longitudinal view 200X, Bright Field.

Figure 6. Same Material as Shown in Figures 3 and 4. Longitudinal view 200X, Polarized Light.

Figure 7. Starting Sheet Given 13% Reduction. Note considerable microcracking. Transverse view 200X, Bright Field.

Figure 8. Same Area as Figure 7. Note low angle grain boundaries and lack of any surface damage. Transverse view 200X. Polarized Light.

Figure 9. Same Material as Figures 7 and 8. Longitudinal view 200X. Bright Field.

Figure 10. Same Material as Figures 7 and 8. Longitudinal view 200X. Polarized Light.

Another characteristic of the foil in Figures 8 and 10 is the smooth, damage-free surface. Some room temperature operations, such as machining, produce heavy surface damage in the form of a type twinning at the edge (Figure 11). This type of damage can be removed by etching off the damaged area. Since room or low temperature rolling does not produce surface damage, no etching to remove surface damage is required.

In summary, it appeared that high surface quality, defect-free foil could be made by rolling provided that the total ductility was not approached since this would cause micro-cracking; and providing that the oxidation temperature of about 800°F was not exceeded.

Annealing

Initial attempts at annealing high purity beryllium foil in production furnace vacuums (1×10^{-6} torr) showed that appreciable oxidation resulting in surface discoloration occurred at any temperature over 1200°F. To find a method of producing foil which avoided significant oxidation of the surface, studies of annealing response at 1200°F for various amounts of cold work were performed.¹ Figure 11 is a plot of the Knoop hardness versus annealing

Figure 11. Beryllium Sheet Given a Heavy Cut Machined Surface. Note acicular type twinning damage. Transverse view 200X. Polarized Light.

time at 1200°F for foil rolled 11% and 20 percent. The results show that for 11 and 20% reduction only partial recovery occurred. Increasing the annealing time at 1200°F does not lower the hardness. Based on extrapolation of the data in Figure 12 it appears that 35 to 40% reduction is necessary in the beryllium before the hardness will approach the fully annealed hardness, if annealing is done at 1200°F.

Other protective devices were tried in an attempt to increase the annealing temperature above 1200°F without oxidizing the foil. The methods and results are shown in Table 2.

In summary, annealing studies showed the following.

- High surface finish, fully annealed foil could be produced if an etch or chemical could be found which removed the oxide formed during annealing well above 1300°F, and which did not pit or roughen the surface.
- High surface finish foil could be produced by annealing at 1200°F, thereby avoiding significant oxidation of the surface. However, in order for this foil to be ductile after annealing at 1200°F it would have to have been rolled 35 to 40% reduction in thickness. It was not possible to reduce the thickness of foil this much, as shown in Figure 1.

Figure 12. Knoop Hardness versus Annealing Time for Beryllium Foil Rolled 11 and 20% and Annealed at 1200°F.

Table 2. Various Protective Systems Tried for Beryllium Anneal to Prevent Oxidation.

System	Temp (°F)	Results
10 ⁻⁸ torr vacuum	1400	Oxidized.
High purity argon	1300	Formed bluish compound.
(Turco-treat)	1300	Could not be removed without scraping.
Commercial coating to prevent oxidation and decarburization.		
10 ⁻⁸ torr vacuum with Ti "getter" chips	1300	The beryllium oxidized preferentially to the titanium.

Etching

A program to find an etching agent which would not roughen the surface was carried out by Chemical Technology Research and Development. Although some improvement over past etching solutions was made, all etches that were tried resulted in roughening of the surface. The basic problem is that any chemical we have tried which will attack the beryllium oxide on the surface of the beryllium

will also attack beryllium. Since the entire oxide layer is not penetrated simultaneously by the etching solution, and the etchant attacks the beryllium faster than the oxide, surface roughness is inevitable.

FINAL INVESTIGATION

Based on the initial findings of the work involving rolling, annealing, and etching, the most feasible method of producing high surface finish foil would be by rolling the foil more than 40% total reduction at temperatures below 800°F, followed by a 1200°F anneal in a 10^{-6} torr vacuum.

It had been noticed that foil rolled at temperatures as high as 800°F came out of the mill at a temperature which allowed hand handling. The rolls were removing the heat from the foil as it was rolled. It was felt that increased ductility could be realized if this heat transfer were reduced.

Heat transfer calculations were done on the system, as shown below.

The heat loss in the rolls

$$\Delta h = k_f A (T_{\text{foil}} - T_{\text{rolls}}) dt \int_{t_1}^{t_2}$$

where k_f = heat transfer constant

A = area of contact of rolls and foil

$dt \int_{t_1}^{t_2}$ = time of contact of a given area of foil with the rolls

For a constant roll speed, $dt \int_{t_1}^{t_2}$ and A are approximately constant.

Then the temperature reduction ΔT in the foil = $-\Delta h/C_p$
where C_p = specific heat of beryllium.

In the temperature range of RT to 1600°F beryllium tensile ductility and reduction of area are proportional to temperature. Assuming there is also a linear relation between rolling ductility and temperature, and using the slope given by data points at roll temperatures of RT and 300°F (where the increase in rolling ductility was 9%)* the extrapolation in Figure 13 is obtained.

*One datum point was obtained with the rolls at 300°F (this was done by torch heating). Increasing the roll temperature from RT to 300°F increases the rolling ductility of the beryllium foil from 20% to 29 percent.

Figure 13. Available Ductility of 0.010-in.-Thick Beryllium Foil Rolled at 800°F as a Function of Roll Temperatures from RT to 800°F.

The extrapolation shows that slightly over 50% total ductility is available with the rolls and the foil both at 800°F. This would allow foil to be rolled enough to allow annealing at 1200°F, with enough rolling ductility left unused to avoid microcracking.

To confirm the calculated data, a heating system utilizing electrical resistance heaters was placed in hollow back up rolls is a 6 in. Stanat Mill as shown in Figure 14. This system was only capable of heating the work rolls to 500°F. High purity beryllium foil was rolled with the rolls at 500°F. Figure 15 shows the experimental values of rolling ductility as a function of foil temperature. Also plotted on Figure 15 are the calculated values of ductility to 800°F. The experimental values are above the calculated ones at roll, at a temperature of 500°F. This shows that the calculated values of available ductility up to 500°F are valid and leads one to expect that the calculated value at 800°F is also close to the actual value, if we had been able to determine it experimentally.

Some experimental work was done to confirm that 40% reduction would indeed allow recovery of sufficient

Figure 14. Heated Roll Setup for Stanat Mill Used in Hot Roll Experiments.

ductility during a 1200°F anneal.** Samples of beryllium foil were rolled various amounts up to 60% in the heated mill. Several of these samples were rolled more than their available ductility and were extensively cracked. For the purpose of this testing, however, small pieces without cracks would suffice.

All samples were annealed at 1200°F for 4 hours. They were then examined visually for surface appearance and were bend tested around a 10T bend radius to evaluate ductility. All samples had a bright, shiny surface appearance. Samples rolled less than 50% did not possess adequate bend

**When a metal is worked, internal defects are produced which decrease the metal's ductility. When enough defects are produced, the metal has no ductility remaining and it will be brittle. When heat is applied there is a tendency to remove the defects, and restore ductility. The actual degree to which defects are removed is a function of the number of defects, the temperature at which they were introduced, and the length of time and temperature at which the metal is heated.

Figure 15. Comparison of Calculated and Experimentally Determined Ductilities of Beryllium Rolled at 800°F through Rolls Heated in the Range from RT to 800°F.

ductility to survive the bend tests. This amount of reduction is a somewhat higher figure than the 40% previously reported in the initial investigation. The 40% figure was determined by investigation of the hardness drop during annealing at 1200°F. It was felt that a partially recrystallized structure (in which the defects are partially removed) would give the foil sufficient ductility, and partial recrystallization is realized with 40%-reduction foil followed by a 1200°F, 3-hour anneal. The bend tests, being an actual measure of ductility, showed that metallographic examination is not an accurate way of determining ductility.

REFERENCE

1. A. W. Brewer, J. G. Avery, and F. J. Fraikor, Recovery in Beryllium Foil, USAEC RFP-1719.

APPENDIX I

Present Procedure for Producing Beryllium Foil

Starting with 0.020-in. foil, which is in the thickness range obtained after hot rolling of beryllium is completed, smaller diameter and higher surface finish rolls are used to roll down to foil thicknesses.

STAGE I

<u>Initial Thickness</u>	<u>Final Thickness</u>	<u>No. of Passes</u>	<u>Surface Finish After Rolling ($\mu\text{in/in rms}$)</u>
0.020 in.	0.018 in.	3	15

Anneal at 760°C – 6 hours, trim off cracked edges, etch in 48% H₂O-4% HF-48% HNO₃ solution to remove oxide. Thickness after etching, 0.016 inch. Surface finish after etching, 70 $\mu\text{in/in rms}$.

STAGE II

<u>Initial Thickness</u>	<u>Final Thickness</u>	<u>No. of Passes</u>	<u>Surface Finish After Rolling ($\mu\text{in/in rms}$)</u>
0.016 in.	0.014 in.	3	15

Anneal at 760°C – 6 hours, trim off cracked edges, etch in 48% H₂O-4% HF-48% HNO₃ solution to remove oxide. Thickness after etching, 0.012 inch. Surface finish after etching, 70 $\mu\text{in/in rms}$.

STAGE III

<u>Initial Thickness</u>	<u>Final Thickness</u>	<u>No. of Passes</u>	<u>Surface Finish After Rolling ($\mu\text{in/in rms}$)</u>
0.012 in.	0.010 in.	3	15

Anneal at 760°C – 6 hours, trim off cracked edges, etch in 48% H₂O-4% HF-48% HNO₃ solution to remove oxide. Thickness after etching, 0.008 inch. Surface finish, 70 $\mu\text{in/in rms}$.

STAGE IV

<u>Initial Thickness</u>	<u>Final Thickness</u>	<u>No. of Passes</u>	<u>Surface Finish After Rolling ($\mu\text{in/in rms}$)</u>
0.008 in.	0.0065 in.	3	15

Anneal at 760°C – 6 hours, trim off cracked edges, etch in 48% H₂O-4% HF-48% HNO₃ solution to remove oxide. Thickness after etching, 0.004 inch. Surface finish after etching, 70 $\mu\text{in/in rms}$.

STAGE V

<u>Initial Thickness</u>	<u>Final Thickness</u>	<u>No. of Passes</u>	<u>Surface Finish After Rolling ($\mu\text{in/in rms}$)</u>
0.004 in.	0.0035 in.	3	10

Anneal in 10⁻⁶ torr vacuum at 760°C, trim off cracked edges, etch in phosphoric acid-H₂O solution to remove light oxide. Thickness after etching, 0.0030 inch. Surface finish 30 $\mu\text{in/in rms}$. (750 ml H₃PO₄ 50 ml H₂SO₄, 50 g CrO₃ with 2000 ml distilled H₂O.)

STAGE VI

<u>Initial Thickness</u>	<u>Final Thickness</u>	<u>No. of Passes</u>	<u>Surface Finish After Rolling ($\mu\text{in/in rms}$)</u>
0.0030 in.	0.0027 in.	3	10

Repeat annealing, etching, and trimming procedures of Stage V. Thickness after etching, 0.0025 inch. Surface finish after etching 30 $\mu\text{in/in rms}$.

STAGE VII

<u>Initial Thickness</u>	<u>Final Thickness</u>	<u>No. of Passes</u>	<u>Surface Finish After Rolling ($\mu\text{in/in rms}$)</u>
0.0025 in.	0.0021 in.	3	10

Final annealing, trimming, and chemical cleaning produce a 0.0020-in.-thick beryllium foil having a surface finish of 20 to 30 $\mu\text{in/in rms}$.