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# **PRODUCTION AND PROCESSING OF Cu-Cr-Nb ALLOYS**

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## **SUMMARY**

A new Cu-based alloy possessing high strength, high conductivity, and good stability at elevated temperatures has recently been produced. This paper details the melting of the master alloys, production of rapidly solidified ribbon, and processing of the ribbon to sheet by hot pressing and hot rolling.

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## **1 INTRODUCTION**

There are many potential applications for materials that possess a combination of high strength, high thermal conductivity and good long term stability at elevated temperatures. To develop a material with this combination of properties, the decision was made to precipitation strengthen Cu with a high melting point intermetallic compound whose constituent elements have unlimited solubility in liquid Cu, but minimal solubility in solid Cu. From the available data, the intermetallic compound  $\text{Cr}_2\text{Nb}$  was selected as the precipitating phase.

This paper deals with the production of the master melts, the rapid solidification processing of the materials, and the consolidation of the rapidly solidified alloys. The master melts were produced by induction melting elemental charges of the desired compositions under an Ar cover gas. Chill block melt spinning (CBMS) was chosen for processing the materials to allow the formation of a supersaturated solution from which  $\text{Cr}_2\text{Nb}$  would be preferentially precipitated. The ribbons produced by CBMS were chopped into flakes which were cold and hot pressed into plates. The plates were reduced 80% in thickness by hot rolling to produce a sheet product.

## **2 EXPERIMENTAL PROCEDURE**

Master alloys of the desired compositions were induction melted. All the alloys were to have an atomic ratio of Cr to Nb of 2 to 1. Cr contents ranged from 2 to 10 a/o, and Nb contents ranged from 1 to 5 a/o.

Elemental charges consisting of oxygen free Cu (2 ppm O), 99.999% pure iodide Cr, and 99.5% pure Nb were induction melted in an 18% porous alumina crucible. An Ar cover gas minimized the volatilization of the elements from the melt. The molten metal was heated to a temperature of  $1538^\circ\text{C}$  ( $2800^\circ\text{F}$ ) or  $100^\circ\text{C}$  ( $180^\circ\text{F}$ ) above the Cu-Nb liquidus of the given Nb composition (1), whichever was higher. The molten metal was held for 10 to 15 minutes at temperature before pouring into a high  $\text{SiO}_2$  alumina shell mold. The master melts produced by the induction melting were remelted during CBMS to produce ribbons of the desired compositions.

For CBMS a sample of the master alloy weighing between 80 and 100 grams was induction melted in a dense alumina crucible (2). An Ircon two-wavelength optical pyrometer measured the temperature of the molten metal. Once the material reached the desired temperature, the crucible was pressurized to 0.069 MPa (10 psi) to eject the molten material through a 1 mm (0.040-in) diameter hole. A Cu heat sink wheel rotating with a surface speed of 20 m/s was used to produce the ribbons. The entire unit was contained in an environmental chamber that had been previously pumped down to a pressure of less than  $5 \times 10^{-5}$  torr and backfilled with Ar. The CBMS produced long, continuous lengths of ribbons.

A previously unreported method for securing the crucible cap that allows reliable sealing was used. The crucible sealing cap allows pressurization of the melt while still enabling viewing of the liquid metal by the optical pyrometer and video camera. Figure 1 shows the cap which consists of a tapered lower section and a flat upper section. The lower section accommodates a rubber stopper bored to accept varying size crucibles. The upper section allows an O-ring assembly to seal a drop-in quartz viewing port. Threaded caps on both the top and bottom of the body force a tight seal when assembled. A pressurization line is joined to the cap through the sidewall.

Figure 2 contains a schematic of the process used to consolidate the ribbons produced. The ribbons were cut into flakes using a Retsch SM-1 rotary grinding mill. A screen at the bottom of the cutting chamber controlled the size of the flakes produced. A screen with an opening size of 4 mm was used for the first pass to convert the long lengths of ribbons to a more manageable form. An intermediate cut with a 2 mm screen before the final cut with a 0.75 mm screen prevented clogging of the cutting chamber. The size distribution of the flakes was determined by measuring optical macrographs of the flakes with a Zeiss Videoplan 2.

Eighty gram samples were vacuum hot pressed at 124.2 MPa (18 ksi) for 1 hour at 650°C (1202°F). A rectangular die with outer dimensions of 5.08 cm X 10.16 cm (2-inches X 4-inches) was used. A ring of 0.3 cm (0.125-inch) stainless steel tubing attached to the die retained the flakes in the die. Plates of oxidized FeCrAlY sheets placed on both flats prevented bonding of the material to the die. To pack the material into the die before hot pressing, the samples were cold pressed using a load of 200 kN (45,000 lbs.). This load produced a nominal stress of 38.8 MPa (5.63 ksi).

The hot pressed plates were reheated to between 920°C (1688°F) and 940°C (1724°F) and hot rolled on a 2-high Fenn rolling mill with 25.4 cm (10-inch) diameter rolls. The final nominal thickness of 0.50 mm (0.020-inch) achieved represents an 80% reduction in thickness. To minimize internal oxidation during the first few passes, a metallic envelope made from 310 stainless steel enclosed the samples. Pieces of Ti sheet placed in the envelope with the samples acted as an O getter to help minimize oxidation further. The envelopes were backfilled with He. After a 30% reduction in thickness, the samples were removed from the envelopes to prevent bonding of the samples to the envelopes. The samples were hot rolled in air to their final thicknesses.

### **3 RESULTS AND DISCUSSION**

During induction melting to produce the master alloys, molds and crucibles showed substantial attack from the liquid metal. There was also a problem with Nb not dissolving into the liquid metal. These results are consistent with the observations of Verhoeven and Gibson (3).

The first problem was solved by examining the alumina-niobia phase diagram (4). The phase diagram shows that above 1560°C (2840°F) any niobia contamination of the alumina results in the formation of a liquid phase. This leads to fluxing of the alumina crucible. It was also observed that the yttria-niobia phase diagram (5) did not exhibit this problem. The addition of niobia to yttria will not result in the formation of a liquid in the temperature range of interest until the niobia content exceeded 50%. The commercially available ZYP type YK yttria paint was used to coat the inner surfaces of both the crucible and molds. To ensure a good bond between the paint and the substrate, the crucibles and molds were heated to 1600°C (2912°F) and 1400°C (2552°F) respectively at a rate of 100°C/hr (180°F/hr), held for 1 hour at temperature, and cooled at a rate of 100°C/hr to room temperature. This solved the problem of the liquid metal attacking the crucible and mold.

The kinetics of dissolving the Nb at temperatures above its liquidus proved to be slow. Holding the molten metal at temperatures between 1538°C (2800°F) and 1704°C (3100°F) for 10 minutes did not dissolve the Nb completely. To circumvent this problem, the larger pieces of Nb were replaced with 0.75 mm (0.030-inch) Nb wire, and the temperature

increased to 1760°C (3200°F) to 1816°C (3300°F). While a few pieces of Nb often remained in the bottom of the crucible following melting, the compositions of the materials showed that almost all the Nb had dissolved into the melt.

Metallographic examination of the cross-sections of the castings revealed the presence of Cr<sub>2</sub>Nb in the as-cast materials. X-ray diffraction analysis of the samples revealed that the Cr<sub>2</sub>Nb was present in its lower temperature FCC form (6). The master alloys were remelted to produce melt spun ribbons.

Initial runs were done by raising the temperature of the alloys to an indicated temperature between 1538°C (2800°F) and 1704°C (3100°F) depending on the composition, followed by metal ejection. Video camera observations of the molten metal revealed that contrary to expectations the Cr<sub>2</sub>Nb had not dissolved in the liquid Cu at these temperatures. Optical microscopy confirmed this observation. Figure 3 shows an undissolved piece of Cr<sub>2</sub>Nb observed in a sample of Cu-10 at.% Cr-5 at.% Nb alloy ejected at an indicated temperature of 1706°C (3102°F). It was determined from observations of the melt that the Cr<sub>2</sub>Nb was stable in liquid Cu up to temperatures approaching the Cr<sub>2</sub>Nb melting point of 1733°C (3151°F) (5). It proved necessary to heat the melts to an indicated temperature of 1871°C (3400°F) to dissolve the Cr<sub>2</sub>Nb into the Cu.

Based on previous experience with Cu-Cr-Ag alloys at NASA Lewis Research Center (2,7), a pressure of 0.069 MPa (10 psi) was selected for CBMS. With the Cu-Cr-Nb alloys this pressure was too high because of the molten metal's good fluidity. Best results occurred at lower pressures between 0.0224 MPa (3.25 psi) and 0.0259 MPa (3.75 psi).

Analysis of the as-melt spun ribbons using transmission electron microscopy (TEM) revealed that the Cr<sub>2</sub>Nb formed in the liquid Cu melt during the melt spinning process (8,9). This phenomenon shows the strong driving force behind the formation of the Cr<sub>2</sub>Nb and the stability of the precipitate phase. The Cr<sub>2</sub>Nb was present in the high temperature hexagonal phase instead of the low temperature FCC form observed in the induction melted master alloys.

One beneficial effect of raising the temperature of the melts was improvement in the uniformity of the ribbons produced. At lower ejection temperatures the free side of the ribbon was very convoluted. With the increased temperature the free side became nearly planar.

A typical optical macrograph of the flakes produced by chopping the ribbons is shown in Figure 4. The larger pieces tended to be thin, elongated flakes. The average maximum diameter of the flakes was near the 0.75 mm size of the final screen.

After hot pressing the material into a plate, the overall densities of the plates were approximately 85% of their theoretical densities. However, the plates had considerable variations in the localized densities of the material. From the results obtained in later tensile testing of the consolidated material, it was discovered that the materials retained yield strengths of more than 100 MPa (14.5 ksi) up to a temperature of 750°C (1382°F). This prevented the full consolidation of the material through hot pressing at 650°C (1202°F). Hot pressing of the flakes should have been done at temperatures between 800°C (1472°F) and 900°C (1652°F). To further consolidate the materials, the plates were hot rolled.

During hot rolling, the rolls, which were not heated, acted to quench the samples as they passed through the rolling mill. The hot pressed plates were therefore reheated to 920°C (1688°F) to 940°C (1724°F) to achieve a rolling temperature above 800°C (1472°F). When initially hot rolled at a lower temperature the samples underwent considerable cracking across the width of the samples. Raising the temperature eliminated the problem of cracking except for minor edge cracking.

An optical micrograph of material hot rolled 30% and decanned is shown in Figure 5. The micrograph shows that the combination of hot pressing and hot rolling was not sufficient to completely consolidate that materials because of their excellent elevated temperature strengths. The optical micrographs does show that the use of the can prevented oxidation of the samples.

Following the decanning of the material, the samples were further reduced for a total of 80% reduction in thickness. An optical micrograph of the cross-section of a fully reduced sample is shown in Figure 6. The micrograph shows that the samples are completely dense. Internal oxidation is, however, a problem since it decorates all the prior particle boundaries and is continuous throughout the sample.

#### **4 CONCLUSIONS**

Cu-Cr-Nb alloys were successfully produced by induction melting and chill block melt spinning. The melt spun ribbons were consolidated by a combination of hot pressing and hot rolling. Full density material was achieved, but internal oxidation was greater than desired, reflecting a need to improve processing. Dynamic consolidation techniques such as extrusion may prove beneficial for achieving full density without continuous oxide layers.

To successfully induction melt the master alloys, it was necessary to use a yttria coating on the crucible and mold. The temperature of the melt also had to be greater than 1816°C (3300°F) because of the slow kinetics of dissolving the Nb into the liquid Cu.

CBMS of the alloys could be done using an Ar atmosphere and a Cu wheel if the temperature of the melt was increased to 1871°C (3400°F) to dissolve the Cr<sub>2</sub>Nb phase in a reasonable length of time.

#### **5 ACKNOWLEDGEMENTS**

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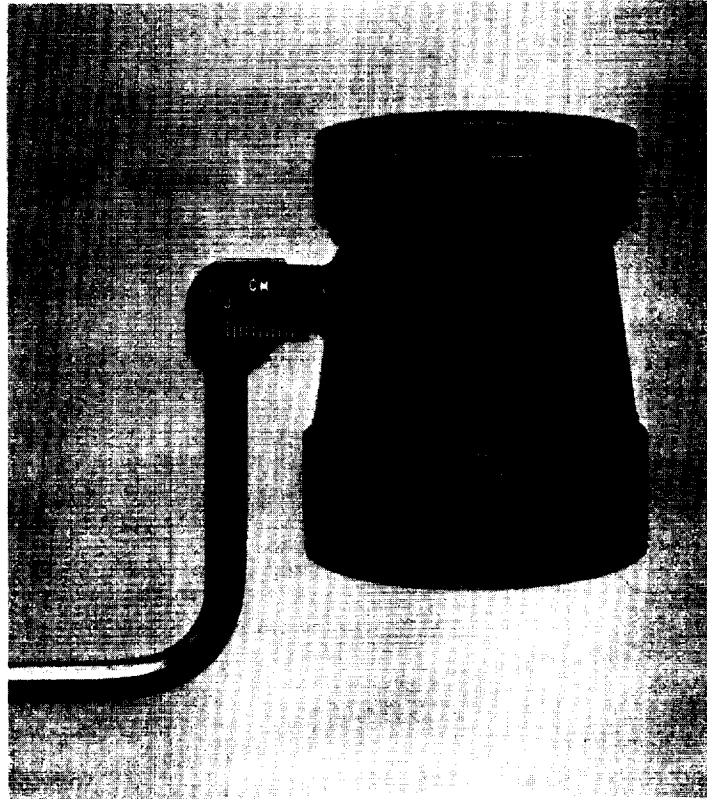
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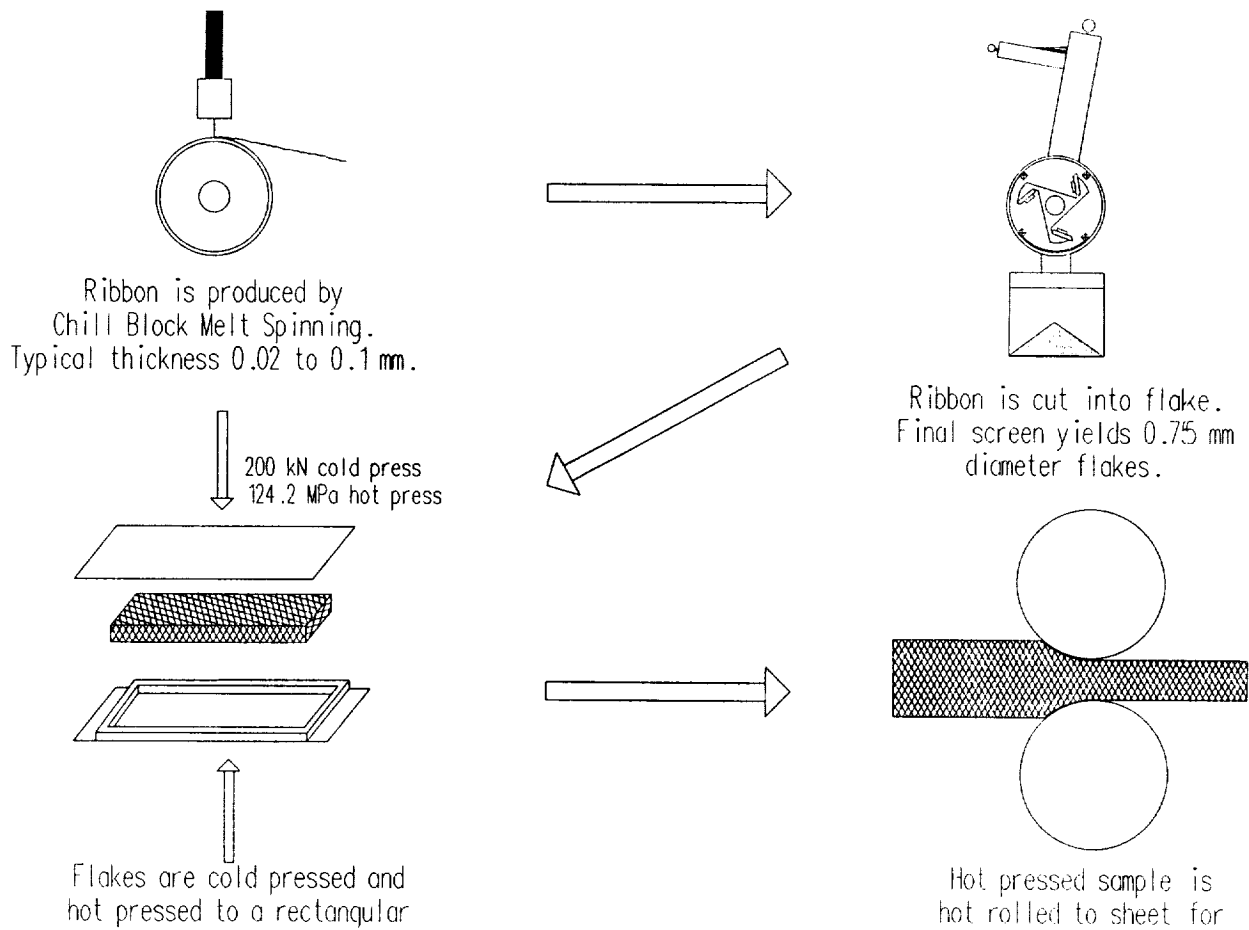
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**Figure 1** - Crucible sealing cap

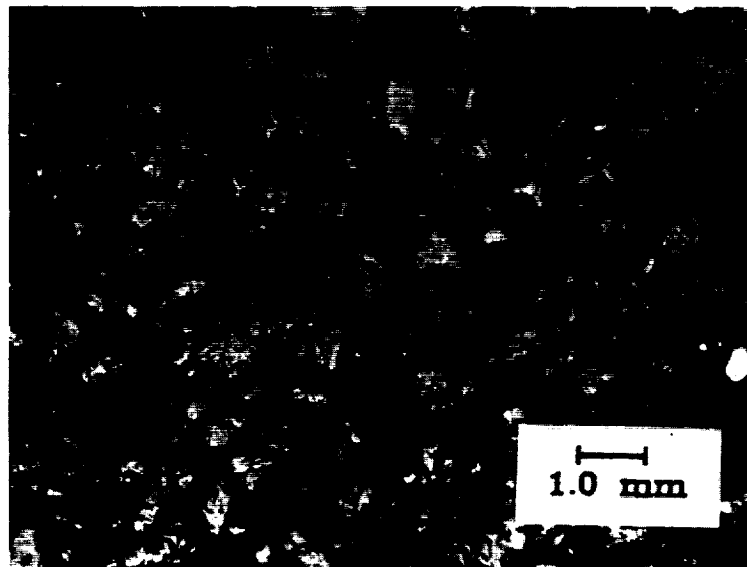


**Figure 2 - Consolidation processing of melt spun Cu-Cr-Nb alloys**

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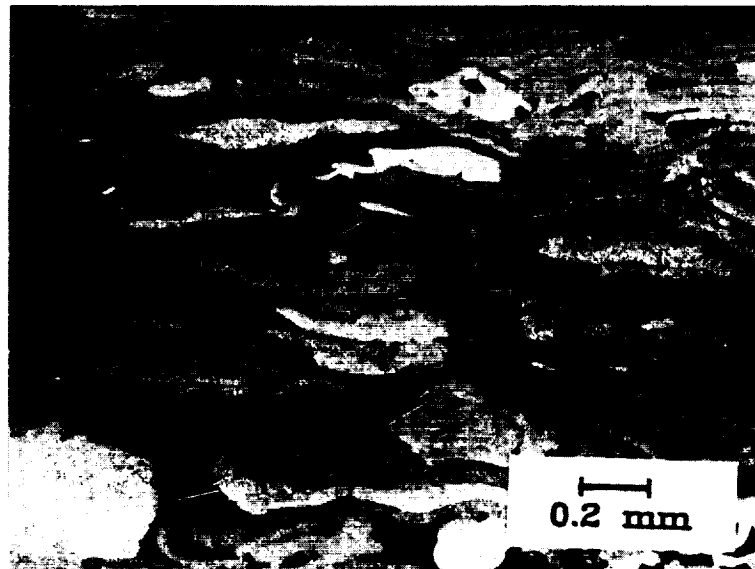
**Figure 3** - Optical micrograph of Cr<sub>2</sub>Nb particle found in as-melt spun ribbon sample



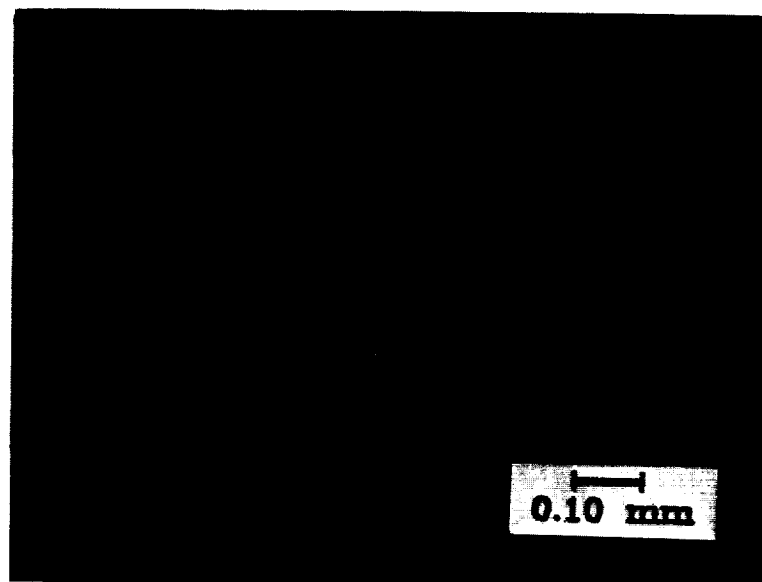
**Figure 4** - Optical macrograph of Cu-Cr-Nb flakes produced by grinding

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**Figure 5** - Optical micrograph of Cu-Cr-Nb plate hot rolled 30% showing little evidence of internal oxidation.  
Arrows denote porosity still remaining in sample.



**Figure 6** - Optical micrograph of longitudinal cross-section of  
Cu-Cr-Nb plate hot rolled 80%.  
Arrows denote internal oxidation in the sample.

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