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Research and Development Report

GROWING NICKEL SINGLE CRYSTALS
BY PULLING FROM A MELT

by

James Herriott, Marlyn Murtha and
George Burnet

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October 1967

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GROWING NICKEL SINGLE CRYSTALS BY PULLING FROM A MELT

James Herriott, Marlyn Murtha and
George Burnet

ABSTRACT

The Czochralski technique was used to grow single crystals of nickel. Crystals ranging in size from 0.06 in. diam and 0.5 in. long to 1.5 in. diam and 9.0 in. long were grown using a NRC crystal pulling unit. Details regarding the procedure used are reported.

INTRODUCTION

The literature contains many references concerning the Czochralski crystal pulling technique¹⁻¹⁷, and also on the growth of single crystals of nickel.¹⁸⁻²¹ There are no references on the growth of nickel single crystals by the pulling technique. This is partially due to the fact that nickel, with a melting point of 1455°C, is near the upper temperature limit of available equipment.

Eighteen nickel crystals were pulled. The crystals ranged in size from 0.06 in. diam by 0.5 in. long to 1.5 in. diam by 9.0 in. long. They were pulled in a vacuum of about 10 μ , at pulling speeds which varied from 0.016 to 0.149 in. per min.

Seven of the 18 samples pulled were single crystals, and five of the last nine attempts resulted in single crystals. The last ten crystals were grown from seeds of a predetermined orientation.

EQUIPMENT

The crystal pulling unit consisted of four basic components: the power supply, the reorder-controller, the pulling chamber, and the vacuum equipment for the pulling chamber. This equipment, purchased from NRC Equipment Corporation, is shown in Fig. 1. Details for the pulling chamber are in Fig. 2.

The melt crucible was heated by a graphite heater which enclosed the crucible assembly. Temperature was controlled by a radiation sensing thermopile located at the base of the hollow crucible assembly shaft. Because rotation produced uniform horizontal temperature gradients, the crucible support shaft and the seed shaft were each turned by a variable speed rotation motor.

The vacuum pumping system consisted of a forepump, a three-stage diffusion pump, and a liquid nitrogen cold trap. Thermocouple gauges were located on each side of the diffusion pump and at the pulling chamber entrance.

Heat losses from the crucible-heater assembly were reduced by use of a double thickness of five mil molybdenum reflector which was supported in a 5/16 in. thick opaque quartz cylinder. Molybdenum and opaque quartz disks were placed above and below the graphite heater to reduce vertical heat losses.

The motor drive on the crucible support shaft provided controlled rotation to 25 rpm, and the height of the crucible could be vertically positioned manually over a 2-3/4 in. range within the graphite heater.

FIGURE 1

Fig. 1. Crystal pulling equipment used for nickel single crystal runs.

DETAILS OF NRC PULLING CHAMBER

FIGURE 2

Fig. 2. Details of crystal pulling chamber.

The seed pulling shaft could be rotated at speeds up to 36 rpm, and the seed positioned initially over a 15-3/4 in. vertical range. The seed shaft vertical drive gear would then uniformly move the shaft up or down at speeds up to 0.15 in. per min. These controls of rotational speeds and vertical movement allowed precise control of the size and shape of the pulled crystal.

CRYSTAL PULLING PROCEDURE

Preparation of Crystal Materials

Proper preparation of the feed and seed material is necessary to give maximum crystal perfection. Material of very high purity is required for growing single crystals of a given orientation.

Two sources of fresh nickel feed material were used. Rod material of 99.95% purity was purchased from the Huntington Alloy Products Division of International Nickel Company Inc. Shot material, 0.25 in. diam, of 99.97% purity was obtained from Belmont Smelting and Refining Works Inc.

Preparation of the nickel materials, as received, for crystal growth consisted of several etching treatments on all surfaces. Composition of the etching baths and the etching times required are given in Table I. The metal was first placed in etching solution No. 1 to remove any oxide film. After being rinsed with distilled water, the sample was placed in etching solution No. 2 which brightened the surfaces. The seed was given a final acetic acid-nitric acid etch (solution No. 3) to determine whether grains were present. The nickel was then stored under methanol until it was placed in the pulling chamber.

Table I. Etch Solutions for Nickel Treatment

Solution No.	Composition	Etching Time
1	133 ml H_2O 62 ml HCl (37.0 wt % HCl) 4 gm. $CuCl_2$	20 to 40 min at 82°C
2	40 ml H_2O 60 ml H_2SO_4 (95.5 wt % H_2SO_4) 90 ml HNO_3 (70.0 wt % HNO_3) let cool and add: 1.2 gm. $NaCl$	5 to 20 sec
3	50 ml HNO_3 (70.0 wt % HNO_3) 50 ml CH_3COOH (99.7 wt % CH_3COOH)	5 to 20 sec

The seed for the first crystal was a 0.25 in. square by 3.75 in. long piece of feed nickel. This seed piece was annealed at 725°C for 15 h and at 600°C for 5 h to increase grain size. The crystal grown from this seed was a nearly equal bi-crystal with vertical division as shown on Fig. 3. Eight crystals were later grown from single crystal seeds spark-cut from halves of this bi-crystal. Some seeds were reused for several pulls. Crystal product and seed data for all runs are given in Table II.

The first few crystals were pulled without an attempt to control orientation. However, by x-ray measurement of the crystals produced, it was determined that seeds with a (100) plane perpendicular to the shaft axis apparently had the best potential for producing single crystals. Seeds with this orientation were used for the last nine runs from which five single crystals resulted.

Preparation of Equipment

After each crystal pull, the portion of the chamber above the graphite heater would be coated with a black deposit. Analysis showed that the deposit consisted of nickel, carbon, and silicone. It was removed with a cleaning powder, "Oakite Highlite" (Oakite Products Inc.; New York, N. Y.), on a damp towel.

Loading the pulling chamber required careful positioning of each movable component. The quartz and molybdenum shields were evenly spaced around the heater to insure uniform heat distribution. The graphite

Fig. 3. A nearly equal bi-crystal grown from an annealed polycrystalline seed.

Table II. Seed and Crystal Properties.

Run No.	Seed		Crystal Condition
	Source	Orientation (Plane Perpendicular) to Growth Axis	
1	annealed feed		B
2	cut from 1		M
3	cut from 1	(100) - 80° to axis	M
4	cut from 1	(100) - 80°	S
5	4 reused	(100) - 80°	M
6	5 reused	(100) - 80°	M
7	3 reused	(100) - 80°	M
8	7 reused	(100) - 80°	S
9	cut from 1	(111)	M
10	cut from 8	(100)	M
11	10 reused	(100)	S
12	11 reused	(100)	M
13	12 reused	(100)	S
14	13 reused	(100)	M
15	14 reused	(100)	S
16	15 reused	(100)	M
17	16 reused	(100)	S
18	Smallest diameter section of 17	(100)	S

M - multicrystal
 B - bi-crystal
 S - single crystal

pedestal-crucible assembly was placed securely on the steel shaft to prevent wobble during rotation. Improper crucible placement would result in non-uniform temperatures and restrict pulling if the crucible was out of line with the seed.

After loading and sealing the chamber, the equipment was degassed at a temperature just below the melting point of nickel. The crucible assembly was positioned at its lowest location inside the heater during degassing. Equipment evacuation required two days to reach a stable pressure of about 10μ .

Operation During Pull

Initial heating of the crucible to 700°C was manually controlled. The heat control was then switched to automatic and the temperature was automatically programmed to the nickel melting temperature. When the feed nickel was melted and the furnace temperature had stabilized, the crucible assembly was raised from its heat-up position to pulling height at which time the top of the crucible was just below the top of the graphite heater. The seed crystal was then lowered until it was immersed 0.25 in. into the melt where it was held for about 5 min during which time that portion of the seed below the melt surface became molten. The pull was then started at a slow speed to insure an established bond between the seed and the melt, and later gradually increased to the desired rate.

Although general rules to be followed resulted from this series of runs, no procedures or requirements were identified which guaranteed set product specifications. Important variables have been determined and controlled, but there are other random factors which seem to significantly effect crystal production.

Initiating crystal growth at a diameter about that of the seed seems to aid in obtaining single crystals. Although both pulling speed and melt temperature control crystal diameter, changes in temperature appeared to have the dominant effect. It was best, therefore, to set the melt temperature and then make small changes by adjusting the pulling speed. When this procedural sequence did not adequately control the crystal diameter profile, the melt temperature was changed and the procedure repeated until the proper melt temperature was reached. On these occasions, it was often necessary to move the seed back into the melt and restart the pull.

At the completion of a pull the temperature was reduced gradually and the vacuum maintained until the equipment was completely cooled. The system was then flushed with argon and opened for inspection of the crystal product.

Methods Used to Determine Results

Care is required when the crystal is removed from the unit. The crystal is heavy, with a thin top section, and it should be kept vertical to prevent bending. After removal, the crystal is placed in a V-shaped holder made from angle iron to allow inspection without causing crystal strain.

Because of the black coating that covered the product from each pull, the crystal was cleaned in etching solution No. 2. This removed all black contaminants but also the surface markings of grain boundaries and striations. The acetic acid-nitric acid etch was used to restore these.

For a crystal with the (100) plane perpendicular to the growth axis, the presence of a single crystal could be detected after etching by observing four reflection planes running vertically down the crystal at 90° intervals. During pulling, these reflection planes could be observed just above the melt and indicate that a single crystal was being grown.

If a crystal showed no defect after etching it was further characterized by x-ray analysis. The Laue back-reflection x-ray method showed the length of the crystal on a line parallel to the growth axis and verified that the original orientation existed for the entire length of the crystal.

CONCLUSIONS

The Czochralski-type crystal pulling unit, shown and described previously, worked satisfactorily in the pulling of nickel single crystals. Success in obtaining single crystal products increased when single crystal seeds of a given orientation were used. Crystals having a (100) plane perpendicular to the growth axis were the easiest to grow.

Modification of the temperature control system would improve the operation of the pulling unit. Consistent production of pulled crystals requires precise control of the melt temperature. The existing system, with a radiation thermopile sensor located approximately two feet from

the crucible assembly does not provide fast-response control. A high-temperature thermocouple located at crucible height would probably improve control of crucible temperature.

To confirm this supposition a brief series of runs was made using a platinum-platinum, 10% rhodium thermocouple in a tantalum tube positioned at crucible height. Unit control was satisfactory until the thermocouple burned out at the feed melting temperature. Development work is planned using a tungsten-rhenium thermocouple, suitable for high temperature operation.

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T.C. - THERMOCOUPLE GAGE
V - HIGH VACUUM VALVE

SEED VERTICAL POSITION MOTOR

SEED ROTATION MOTOR

STAINLESS STEEL BELL JAR

POSITION & ROTATION CONTROLS

THERMOCOUPLE GAGE BOX

ARGON FLUSH TANK

VACUUM CONTROL SECTION

DIFFUSION PUMP

WELCH FOREPUMP

V-1

V-2

V-3

V-4

COLD TRAP

T.C.-1

T.C.-2

T.C.-3

PULLING CHAMBER

RECORDER

HEAT CONTROL

RECORDER & CONTROL PANEL

NRC

THERMOPILE

HEATER POWER SUPPLY

CRUCIBLE ROTATION MOTOR

T.C. - THERMOCOUPLE GAGE
V - HIGH VACUUM VALVE

SEED VERTICAL POSITION MOTOR

SEED ROTATION
MOTOR _____

STAINLESS STEEL
BELL JAR —

POSITION & ROTATION CONTROLS

**THERMOCOUPLE
GAGE BOX** →

ARGON FLUSH TANK

VACUUM CONTROL SECTION

DIFFUSION PUMP

WELCH
FOREPUMP

COLD TRAP

PULLING CHAMBER

T.C.-3

T.C.-2

TC-1

CRUCIBLE ROTATION MOTOR

HEATER POWER SUPPLY

VOLTS AMPS

RECORDED

HEAT CONTROL

RECORDER & CONTROL PANEL

- THERMOPILE

"CZOCHELSKI" NICKEL CRYSTAL GROWING EQUIPMENT

FIGURE 1

26.

DETAILS OF NRC PULLING CHAMBER

FIGURE 2

Fig 3