

# Mold Manufacture with Plasma Spraying

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A process has been developed to produce molds or tooling using a steel or chrome-plated steel model. The investigation examined the effect of coating and model materials, model temperature and spray angle on the coating separation from the model surface, coating delamination, and surface quality. A polished model disk was heated and then plasma sprayed with iron, nickel, Ni-Al, or Ni-Cr-B-Si. It was found that the minimum temperature to facilitate entire coating removal was lower for steel models and varied between 200 and 450 °C depending on the material. However, at higher temperatures the higher bond strength produced by oxidation on the steel resulted in significant coating pullout. A chrome-plated model, heated to 600 to 700 °C, is required to produce a defect-free coating. The effect of substrate angle on open porosity is most critical for the Ni-Cr-B-Si alloy and least important for Ni-Al coatings. The surface roughness of the plasma-sprayed molds is comparable to the corresponding models, permitting good surface detail reproducibility. Several molds and tools were produced for use in the glass, rubber, and plastics industries.

Keywords	adhesion, coating removal, molds, plasma spraying,
	porosity, roughness, tooling

### 1. Introduction

THE MANUFACTURE of components typically requires a forming or shaping stage. This is accomplished with molds, tooling, or dies. Several routes are available for producing molds, including pressing, electroforming, electrical discharge machining, chemical erosion, precision casting, and machining (Ref 1). Plasma spraying is another technology requiring few manufacturing stages to produce molds with complicated surfaces and precise dimensions (Ref 2). This process reduces tooling costs; thereby supporting shorter production runs for a larger variety of products and permits quick manufacture of prototypes. The method can produce irregularly shaped parts, providing an excellent copy of surface detail and maintaining precise form and dimension.

The desired outcome of metal spraying is adhesion of the coating material onto the model surface during spraying and separation of the deposited material after spraying to produce a surface finish identical to the model surface: a smooth, nonporous deposit without cracks and de-adhered regions. Metal spraying has been used since the early 1970s, when it was discovered that thin shells of zinc and zinc-tin could be sprayed onto models of wood, plastic, and other materials (Ref 3). Molds with a larger surface could be prepared for applications requiring low pressures and temperatures, such as in the plastics industry.

# 2. Thermal Spraying Approach

The preparation of metal-spray tooling consists of five steps. In step 1 a model is produced by stereolithography (Ref 4) or machining or is crafted by hand to a smooth surface with dimensions of the desired end product. It is then covered with a hightemperature barrier coat (step 2) to protect the model and a parting agent, such as polyvinyl alcohol, to promote release of the model when the tool is finished. The model is covered with a metallic coating about 1 to 3 mm thick using metal spraying (step 3). At this stage the coating is very flexible and needs support. To give the thin shell rigidity and ensure that no change in dimension occurs during handling, the mold is framed (step 4) and then a backup material is applied (step 5).

An excellent surface finish can be achieved by spraying lowmelting-point materials such as tin or Kirksite (a zinc-base alloy; TAFA, Inc., 146 Pembroke Road, Concord, NH 03301) onto glass, poly (methyl)methacrylate, polycarbonate, polypropylene, or polyimide (Ref 5). Accurate surface replication, however, is dictated by melting or deformation of the pattern material. Use of copper, steel, and aluminum is difficult to apply onto models because of high melting temperatures and shrinkage rates. Weiss et al. (Ref 6) overcame this difficulty by using a tin-alloy-coated model onto which plasma-sprayed stainless steel superficially melted the tin to create good adhesion, thereby overcoming problems of coating warpage and delamination. Again, accurate surface replication is limited by melting of the tin alloy. Control of the surface temperature with air cooling is important to avoid excessive expansion and melting of the tin alloy.

Use of a steel model offers another alternative for producing molds or tooling. Loss of model shape from melting is no longer an issue, allowing high tool or mold performance materials to be sprayed in addition to producing a support or backing material using the same process. The model can be heated to high temperatures, which offers several advantages. Deposition of the molten droplets onto hot substrates produces well-formed lamellae with lower coating porosity (Ref 7) and higher deposition efficiency (Ref 8). The requirement of a smooth surfacedecreases the number of "stringers" or secondary splashes and is necessary in order to impart smoothness to the mold inner surface. After deposition of the first material layer, another material with a similar coefficient of thermal expansion can then be sprayed to provide support to the mold after removal. Furthermore, once the mold or object has been produced,

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no further operations are required. This paper will show how the surface replication depends on the coating material, substrate material, substrate temperature, and deposition parameters.

### 3. Experimental Procedures

### 3.1 Materials

Steel (Fe-0.45C) was chosen as the model material. Coating materials with a coefficient of expansion similar to the substrate were selected to avoid coating delamination during the cooling process. Iron, nickel, Ni-20Al and Ni-Cr-B-Si (with a composition of 8 to 14 wt% Cr, 2 to 3 wt% B, 1 to 3 wt% Si, and a balance of nickel) were the spray materials. The latter three materials were chosen for their applicability in high-temperature (>700 °C) operating conditions. Nickel has good corrosion resistance and has been used previously for compression and injection molding of plastics (Ref 9). The Ni-Cr-B-Si superalloy has good abrasion, corrosion, and oxidation resistance (Ref 10) and is employed for protection against corrosion and wear of machine parts (Ref 11). Boron and silicon in the alloy provide better flow characteristics of the molten particles, producing denser coatings.

The iron and nickel powders, obtained from metallurgical factories in Ukraine and Russia, were irregular in shape. The Al-Ni and Ni-Cr-B-Si, plasma spraying powders with a spherical morphology, were from Russia and Ukraine, respectively. The Ni-Al powder consisted of nickel encapsulated in aluminum. A mechanical mixture of iron and copper was sprayed as the backing material for the mold support. Powders were classified by sieving to a particle size range of 30 to 80  $\mu$ m for nickel, but 40 to 100  $\mu$ m for the other materials.

Steel was chosen as a model material due to its availability and good machinability. Models were manufactured in the form of disks (see section 3.3) and polished to a surface finish of 0.05  $\mu$ m. A chrome plating (~10  $\mu$ m thick) was electrochemically applied to the models by electroplating.



Fig. 1 Fixture for determining the minimum model temperature for adhesion of the coating to the model disk

### **3.2** Spraying Conditions

A custom-built plasma torch with a 6 mm internal anode diameter was used for plasma spraying. The power level was set to 28 to 31 kW with 350 A and 80 to 90 V. Technical-grade argon (Ar-15N<sub>2</sub>) was used as the primary plasma gas, and hydrogen (10 to 15%) was added to increase the plasma enthalpy. The powder was delivered to the torch at 2 to 5 kg/h, and spraying was conducted at a standoff distance of 10 cm.

#### 3.3 Evaluation Methods

The first stage of the investigation involved obtaining good attachment of the coating during the spraying process followed by entire coating removal from the model surface. It is known that coating adhesion depends on the roughness of the surface to be coated. Spraying onto a rougher surface generally produces a strong attachment (Ref 12). Adhesion on polished surfaces is minimal and the coating can undergo fragmentation and warpage during the spraying process. Heating the substrate surface enhances the coating adhesion. Disks (30 by 80 mm diam) polished to a surface roughness of  $0.05 \,\mu\text{m}$  were heated in a muffle furnace for about an hour and placed onto a thermally insulating layer in the fixture (Fig. 1). A 2 to 3 mm thick coating was immediately sprayed onto the model to determine the minimum temperature for uniform coating adhesion. This was repeated at higher temperatures in 50 °C increments until the coating did not deform during the spraying process. Coatings were produced on steel and chrome-plated surfaces. In this fashion, the temperature at which a uniformly adhered coating is formed could be determined. The temperature of the metal surface was measured by a thermocouple positioned 1 mm behind the front face of the metal plate.

The second stage of the investigation determined the processing parameters that ensure a good coating finish after separation from the model. A disk, smaller in size than previously used



Fig. 2 Experimental arrangement for preparing coatings for surface examination

(5 by 30 mm diam), was placed onto a cylindrical base and fixed with a screw through a cylindrical sleeve (Fig. 2). The temperature of the disk was measured with a thermocouple. The top surface of the sleeve was sandblasted to ensure adhesion of the coating at lower substrate temperatures. After depositing a 2 to 3 mm thick coating, the cylindrical base was removed by releasing the grub screws through the sleeve. The coated disk was then separated from the sleeve, and finally the coating was removed from the disk for further inspection of the underlying surface. The underlying coating surface could then be assessed as a function of substrate temperature. Surface examination for porosity and pullout from the coating was conducted with an optical stereomicroscope and a profilometer.

The contoured surfaces of molds may alter the quality of the deposit. A third experiment determined the dependence of spray angle on the surface porosity of the coating for all the materials. A total of 12 regions, in groups of three each, were placed together to form the test piece. Each region consisted of an area machined to different angles (Fig. 3). The model assembly thus presented panels inclined at angles ranging from 10 to 90° to the oncoming molten particles from the plasma. All four stages were held together by a single fastener. The temperature was measured by a thermocouple inserted into the end stage. Coating porosity was measured using an optical microscope set to a magnification of  $100\times$ .

### 4. Results and Discussion

### 4.1 Replication of Surface Geometry

Coating conformity and ease of removal are important with respect to replicating the surface of the pattern. Spraying onto a cold surface results in peeling of the coating, which begins at the side of the disk and progresses toward the center. During this process of separation, the coating cracks due to the thermally induced stresses and separates from the pattern.

Uniform adhesion of the coating to the disk substrate is observed only at elevated temperatures. Heating the steel model to 150 to 200 °C produces better adhesion to the disk. The minimum temperature for uniform adhesion depends on the model and coating material. The Ni-Al coating on steel requires the lowest model temperature of 200 °C (Fig. 4). This could be attributed to the exothermic behavior during solidification, which



Fig. 3 Test block made up of 12 regions, with four groups of three planes. Angles shown decrease from  $90^{\circ}$  in increments of  $8^{\circ}$ . The side view (extended horizontally for clarity) shows the positioning of the thermocouple within the block.

assists in relieving process-induced stresses. Iron, nickel, and Ni-Cr-B-Si coatings require a preheat of 300 to 450 °C to form an adhering coating. The Ni-Cr-B-Si alloy has a high sensitivity to cracking and exfoliation caused by residual stresses and thus requires a high model temperature (Ref 13). All coatings produced at the given temperatures display a grayish appearance, which suggests a porous surface. Significant pullout was observed for nickel and Ni-Al coatings.

Chrome-plated surfaces require a slightly higher substrate temperature ( $\sim 50$  °C) to facilitate coating removal (Fig. 4). Coatings contain less porosity, observed as a lighter gray appearance, and can be separated with ease from the substrate, with the exception of Ni-Al.



Fig. 4 Minimum model temperature at which a 2 to 3 mm thick coating does not separate from a steel and chrome-plated steel model



**Fig. 5** Coating porosity as a function of spray angle for iron, nickel, Ni-Al, and Ni-Cr-B-Si coatings. The porosity is expressed in terms of a percentage of the total surface area.

# 4.2 Coating Porosity and Pullout

The surface finish of the coating is equally important for the manufacture of a smooth mold. One means of analyzing the surface finish is by measuring pore content and degree of pullout from the coating surface. The pore content, measured by optical microscopy, appears to decrease with hotter substrate temperatures. Above 300 °C, the splat morphology changes from a starshaped to a regular disklike morphology. This has been reported for both metals and ceramics in other studies (Ref 7, 14). A further increase in temperature to about 700 °C could then promote further spreading, which decreases the porosity content. A comparison between the steel and chrome-plated steel model shows that the porosity levels are always lower on chrome-plated surfaces. This can be explained by the higher thermal resistance (Ref 15) of the steel model created by the oxidized surface.

The amount of pullout depends on the model temperature, coating, and model material. This is observed on the coating surface as darker gray areas and/or on the model surface as deadhered coating fragments. For alloyed coatings, pullout decreases to very low levels at elevated temperatures (Table 1). Metals such as iron and nickel generally exhibit more adhesion with the model surface. Matting and Steffens (Ref 16) reported partial welding of plasma-sprayed iron and nickel deposits with the grit-blasted steel base. This partial welding to the roughened surface promotes adhesion. Spraying iron and nickel onto a smooth steel base also showed bonding (Table 1). The amount of pullout increased at higher temperatures. Analysis of the coating with x-ray diffraction after removal from the model showed the presence of iron oxide or metallic compounds formed by diffusion of metallic species across the coating/model interface (Ref 17). The pullout is thought to arise from a reaction between the metal particles and the oxidized substrate.

Steel cannot be used as a model material at 600 to 700 °C unless it is heated in an oxygen-free furnace and sprayed with a shroud (Ref 18) also used in welding technology (Ref 19). This, however, is a costly and time-consuming procedure. By using a chrome-plated surface, pullout can be avoided. Deposition of iron, nickel, Ni-Cr-B-Si, and Ni-Al materials onto chrome-

Table 1 Characterization of model and coating surfaces

plated steel surfaces heated to 600 to 700 °C results in smooth, reflective, nonporous surfaces that replicate the model surface.

#### **4.3** Substrate Angle and Porosity

Mold production requires molten particles to impinge onto surface features at different orientations to build up the functional coating. Figure 5 shows the effect of substrate angle on the coating open porosity for the various materials. Spraying angle is most critical for Ni-Cr-B-Si feedstock. Increased porosity levels are observed for substrates inclined at 40°. Comparison with results from other studies is difficult since bulk porosity is conventionally measured. Smith et al. (Ref 20) plasma sprayed copper, alumina, molybdenum, Ni-5Al, and aluminum onto grit-blasted substrates and showed increased coating roughness, lower deposition efficiency, and increased levels of porosity beginning at a similar angle. Montavon et al. (Ref 21) examined Astroloy (Ludlow-Saylor, Warrenton, MO) splats sprayed onto polished copper substrates heated to 850 °C and reported splashing at 60°. These observations suggest that porosity arises both from the shadowing effect at larger angles and from splashing.

The optimal spraying angle on chrome-plated steel models is 40 to 90° for iron at 600 °C, 45 to 90° for nickel at 700 °C, 50 to 90° for Ni-Cr-B-Si at 700 °C, and 35 to 90° for Ni-Al coatings at 700 °C. Spraying angles less than those specified will produce increased porosity, leading to a poor surface finish and hence a lower mold performance.

#### 4.4 Surface Quality

The nickel coating separated from a chrome-plated steel model was chosen for surface roughness assessment. Roughness, measured as the peak-to-valley value  $R_z$ , was determined both on the coating and model surfaces. Evaluation of both surfaces indicated that the change in roughness was more easily detected on the coating. At 550 °C, the surface roughness of the coating and the model was 2.7 and 1.0  $\mu$ m, respectively. These values suggest that small segments, probably loosely bonded lamellae, were transferred from the coating to the model surface.

		Model surface		Coating surface	
Coating material	Chrome plated	Temperature, °C	Adhered coating, %	Pore content, %	Pullout, %
Iron	No	300	23-33	3-7	23-33
	No	570	42-54		42-54
	Yes	350	<1		<1
	Yes	550			
Nickel	No	350	8-15	3-5	8-15
	No	600	70-80	<1	70-80
	Yes	450	<1	1	<1
	Yes	700			
Ni-Cr-B-Si	No	450	<1		<1
	No	700			
	Yes	450	2		2
	Yes	700			
Ni-Al	No	350	15-20	3-5	15-20
	No	650	<1	1-2	<1
	Yes	450	8-18		8-18
	Yes	650	3-7		3-7
	Yes	700	<1		<1

An increase in temperature by 50 °C produces a slightly smoother surface. The surface roughness continued to decrease for higher model temperatures (Fig. 6). Heating the model to 700 °C is required to obtain a mold surface that is comparable to the model surface.

### 4.5 Manufacture of Molds

Tooling requires a backing or support material for rigidity. A support layer is added while the coating is still hot after the model has been entirely covered with the functional coating.

## **MODEL SURFACE**

The second layer can be as thick as 1 to 2 cm in cases where mechanical strength is required. Typically, a mixture of iron and copper is plasma sprayed onto the first coating layer. This material combination is chosen for ease of machinability. The entire coating operation can take as little as 40 min to produce a mold, depending on the complexity and size of the pattern. For example, to produce a simple cylinder with an internal diameter of 15 mm, a wall thickness of 5 mm, and a length of 200 mm requires a total spraying time of 1 h. The mold is then separated from the model while hot and later machined to the final dimensions. A cross section of a coating assembly, where the coating was not



Fig. 6 Surface profiles of the model and coating surfaces after spraying at 600, 650, and 700 °C. The surface of the model before spraying is shown for comparison. Error in  $R_z$  is  $\pm 0.02$ .



Fig. 7 Micrographs of the coating assembly showing the model, coating, and support material. (a) Chrome-plated model. (b) Steel model

removed from the model, is shown in Fig. 7. The dark interface between the model and the nickel coating in Fig. 7(b) represents the oxide layer, but the bright layer in Fig. 7(a) is the chrome plating.

Circular patterns can be placed in a lathe. This produces a thicker functional layer in areas with a smaller diameter. A larger coefficient of thermal expansion of the model material will allow the model to separate from the mold if a one-piece mold is to be produced. Separation of the model may need to be carried out while the coating is still hot. To aid the separation of the model from the coating, some models may need to be assembled in different parts so that they can be removed separately. Individual components can be removed with little effort, which is necessary when more complicated molds are manufactured. The adhesion of the coating on the model depends on the coating material but typically varies between 2 and 5 MPa. This low adhesion strength will lead to a clean model surface and good surface reproducibility in those situations where the cohesive strength of individual flattened particles is not reduced by porosity. The bond strength for the different materials together with other optimal spraying conditions are shown in Table 2. Considering issues such as good coating conformity, surface quality, and ease of coating removal, the best coating material for mold manufacture has been found to be nickel on a chrome-plated model surface. Other materials such as iron and Ni-Al are more flexible in obtaining good coating density on complicated surface features.

Matched die or mold halves are important to avoid excessive flash during molding operations. The separation of the mold

from the model enables it to be used for the production of the second half. The production of matching molds ensures proper alignment of both halves.

The molds prepared by plasma spraying have been used in industry (Ref 22) for producing wax, plastic, rubber, and glass objects. Models, together with the plasma-sprayed molds, are shown in Fig. 8. The left pair in Fig. 8(a) is used to manufacture the stem of a glass, and the right pair is used to make a plastic screwdriver handle. Figure 8(b) shows applications where the surface replication is more critical. In the upper left is one-half of the mold used to make rubber wheels for toys, and the lower mold is used to make candles.

## 5. Conclusions

This study has developed coating parameters—such a model material, surface temperature, and spraying angle—which are required for building up a coating that does not deform during the coating process and can be removed with a surface roughness comparable to the original model surface roughness.

Metallic molds from iron, nickel, Ni-Al, and Ni-Cr-B-Si can be produced by air plasma spraying onto steel and chromeplated steel models. The main processing criterion is the model temperature. Model surfaces must be heated above 400 °C to avoid coating warpage and fragmentation, but heating to 600 to 700 °C is required to remove coating porosity and reduce coating pullout. Small spray angles can also introduce surface porosity. Spray angular ranges are the most flexible for Ni-Al and iron

Table 2 Process parame	eters for producing	molds or dies usin	g a chrome-plated model
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Powder composition	Particle size, µm	Model temperature, °C	Spray angle, degrees	Bond strength, MPa
	40-100	600	35-90	5
Nickel	30-80	700	45-90	2
Ni-Cr-B-Si	40-100	700	50-90	2
Ni-Al	40-100	700	35-90	1-2



(a)

(b)

Fig. 8 Molds for producing commercial items. (a) Molds with their respective models used for producing drinking glass stems and plastic screwdriver handles. (b) Molds for making rubber wheels for toys and wax candles. The coin shown is 2.2 cm in diameter.

coatings, allowing more complex molds to be sprayed. Oxidation of steel promotes bonding of the sprayed material and is therefore not recommended. Steel models require chrome plating to prevent coating pullout.

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### References

- W.F. Robb, Tool-Making Processes, Equipment and Methods, *Plastics Mold Engineering*, J.H. DuBois and W.I. Pribble, Ed., Reinhold, 1965, p 148-180
- 2. A. Kovalevskis and G. Balasnikovs, Method for Producing Moulds, USSR Patent 369183, 1965
- L. Grant, Sprayed Metal Molds, Handbook of Plastic Materials and Technology, K.L. Mittal, Ed., John Wiley & Sons, 1990, p 1425-1433
- 4. S. Ashley, Rapid Prototyping for Artificial Body Parts, *Mech. Eng.*, Vol 5, 1993, p 50-53
- K.M. McHugh, Materials Processing with de Laval Spray-Forming Nozzles: Net-Shape Applications, *Thermal Spray Industrial Applications*, C.C. Berndt and S. Sampath, Ed., ASM International, 1994, p 477-483
- L.E. Weiss, D.G. Thuel, L. Schultz, and F.B. Prinz, Arc-Sprayed Steel-Faced Tooling, J. Therm. Spray Technol., Vol 3 (No. 3), 1994, p 275-281
- R.C. Dykhuizen, Review of Impact and Solidification of Molten Thermal Spray Droplets, J. Therm. Spray Technol., Vol 3 (No. 4), 1994, p 351-361
- D.G. Moore, A.G. Eubanks, H.R. Thornton, W.D. Hayes, and A.W. Cigler, "Studies of the Particle-Impact Process for Applying Ceramic and Cermet Coatings," AD-266381, National Bureau of Standards, Aug 1961
- 9. P. Spiro, Hard Nickel Electroformed Moulds, *Int. Plast. Eng.*, Vol 2 (No. 8), 1969, p 359-361
- A.P. van Petegheim and H.F. Demyere, Metal Spraying and Melting of Ni-Cr-B-Si Alloys for Increased Abrasion, Corrosion and Oxidation Resistance, *Rev. Soudure*, Vol 20 (No. 2), 1964, p 96-107 (in French)

- 11. N. Klein, Fusible Hard Flame Spray Materials for Wear and Corrosion Protection, *Schweissen Schneiden*, Vol 16 (No. 10), 1964, p 472-476 (in German)
- C.C. Berndt and C.K. Lin, Measurement of Adhesion for Thermally Sprayed Materials, J. Adhes. Sci. Technol., Vol 7 (No. 12), 1993, p 1235-1264
- Y. Longa and M. Takemoto, High Temperature Corrosion of Laser-Glazed Alloys in Na<sub>2</sub>So<sub>4</sub>-V<sub>2</sub>O<sub>5</sub>, *Corrosion*, Vol 48 (No. 7), 1992, p 599-607
- L. Bianchi, F. Blein, P. Lucchese, M. Vardelle, A. Vardelle, and P. Fauchais, Effect of Particle Velocity and Substrate Temperature on Alumina and Zirconia Splat Formation, *Thermal Spray Industrial Applications*, C.C. Berndt and S. Sampath, Ed., ASM International, 1994, p 569-574
- M. Pasandideh-Fard and J. Mostaghimi, On the Spreading and Solidification of Molten Particles in a Plasma Spray Process: Effect of Thermal Contact Resistance, *Plasma Chem. Plasma Process.*, Vol 16 (No. 1), 1996, p 83S-98S
- A. Matting and H.D. Steffens, Contribution to the Study of Electric Arc Metal Spraying Process, Z. Metallkd., Vol 53 (No. 2), 1962, p 138-144 (in German)
- A. Kovalevskis, "Investigation of Mould Production Appliances with Plasma Spraying," Ph.D. dissertation, Byelorussian Institute of Agriculture, 1974 (in Russian)
- A. Kovalevskis, Preparation of Moulds with Plasma Spraying, Progressive Methods for Producing Technical Appliances, I. Tarasov, I. Mochulski, and B. Birin, Ed., Technical Research Information Institute, Riga, 1969, p 50-66 (in Russian)
- 19. E.F. Gorman, New Developments in Gas Shielding, Weld. J., Vol 41 (No. 8), 1962, p 728-734
- M.F. Smith, R.A. Neiser, and R.C. Dykhuizen, An Investigation of the Effects of Droplet Impact Angle in Thermal Spray Deposition, *Thermal Spray Industrial Applications*, C.C. Berndt and S. Sampath, Ed., ASM International, 1994, p 603-608
- G. Montavon, C. Coddet, S. Sampath, H. Herman, and C.C. Berndt, Vacuum Plasma Spray Forming of Astroloy: An Investigation of Processing Parameters, *Thermal Spray Industrial Applications*, C.C. Berndt and S. Sampath, Ed., ASM International, 1994, p 469-475
- 22. A. Kovalevskis, Christmas Tree Moulds from Temperature Resistant and Conducting Materials for Automated Production Lines, *Toy Manuf.*, Vol 5 (No. 11), 1971, p 4-5 (in Russian)