Title: Improved Tubulars for Better Economics in Deep Gas Well Drilling using Microwave Technology

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1. Executive Summary

The objective of the research program has been to improve the rate-of-penetration in deep hostile environments by improving the life cycle and performance of coiled-tubing, an important component of a deep well drilling system for oil and gas exploration. The current process of the manufacture long tubular steel products consists of shaping the tube from flat strip, welding the seam and sections into lengths that can be miles long, and coiling onto reels. However, the welds, that are a weak point, now limit the performance of the coil tubing. This is not only from a toughness standpoint but also from a corrosion standpoint. By utilizing the latest developments in the sintering of materials with microwave energy and powder metal extrusion technology for the manufacture of seamless coiled tubing and other tubular products, these problems can be eliminated. The project is therefore to develop a continuous microwave process to sinter continuously formed/extruded steel powders. In order to begin the program quickly, three paths of investigation were started. They were metal powder composition development, process/equipment development, and extrusion development. This is a summary of Phase I extension of the three-phase program. The technical progress report for the Phase I was submitted last year. That report had provided details of technical progress achieved that time. This annual progress report gives a details of the technical progress made during the extension period of Oct. 2003 to Feb. 2005.

The main purpose of this extension period was to complete the feasibility study of extrusion process of steel powder and continuously sinter the extruded tubing. The research program has been based on the development of microwave technology to process tubular specimens of powder metals, especially steels. The existing microwave systems at the Materials Research Laboratory (MRL) and Dennis Tool Company (DTC) were suitably modified to process tubular small specimens. The precursor powder metals were either extruded or cold isostatically pressed (CIP) to form tubular specimens.

After conducting an extensive and systematic investigation of extrusion process for producing long tubes, it was determined that there were several difficulties in adopting extrusion process and it cannot be economically used for producing thousands of feet long green tubing. Originally, it was proposed to accomplish the goals of this program by developing an efficient and economically viable continuous microwave process to sinter continuously formed/extruded

steel powder for the manufacture of seamless coiled tubing and other tubular products. However, based on the results and faced with insurmountable difficulties in the extrusion and de-waxing processes, the approach of achieving the goals of the program should be changed. It is recommended that an approach of microwave sintering combined with Cold Isostatic Press (CIP) and joining (by induction or microwave) should be adopted. This process can be developed into a semi-continuous sintering process if the CIP can produce parts fast enough to match the microwave sintering rates.

2. Abstract

Technical Objectives: The main objective of the research program has been to improve the rate-of-penetration in deep hostile environments by improving the life cycle and performance of coiled-tubing, an important component of a deep well drilling system for oil and gas exploration, by utilizing the latest developments in the microwave materials technology.

Originally, it was proposed to accomplish this by developing an efficient and economically viable continuous microwave process to sinter continuously formed/extruded steel powder for the manufacture of seamless coiled tubing and other tubular products. However, based on the results and faced with insurmountable difficulties in the extrusion and de-waxing processes, the approach of achieving the goals of the program has been slightly changed. In the continuation proposal an approach of microwave sintering combined with Cold Isostatic Press (CIP) and joining (by induction or microwave) is adopted. This process can be developed into a semi-continuous sintering process if the CIP can produce parts fast enough to match the microwave sintering rates.

Originally, the entire program was spread over three phases with the following goals:

Phase I: Demonstration of the feasibility concept of continuous microwave sintering process for tubular steel products.

Phase II: Design, building and testing of a prototype microwave system which shall be combined with a continuous extruder for steel tubular objects.

Phase III: Execution of the plan for commercialization of the technology by one of the industrial partners.

However, since some of the goals of the phase I were not completed, an extension of nine months was granted and we continued extrusion experiments, designed and built semi-continuous microwave sintering unit.

3. Experimental

The research program has been based on the development of microwave technology to process tubular specimens of powder metals, especially steels. The existing microwave systems at the Materials Research Laboratory (MRL) and Dennis Tool Company (DTC) were suitably modified to process tubular small specimens. The precursor powder metals were either extruded or cold isostatically pressed (CIP) to form tubular specimens. The procedure for making trial samples and modifications made in the microwave systems are described below:

i. Modification of Microwave systems: The existing vertical continuous microwave systems at MRL and DTC had been used in the past for the processing of ceramics and WC/Co parts. To process powder metal (steel) samples the systems at MRL and DTC were suitably modified by designing and installing new insulation packages and tube assembly, etc. As the experiments progressed to be executed further modifications were required to facilitate the smooth movement of crucibles and long steel tubes of diameter >1.5 inch. Also some necessary modifications were made in the insulation package and microwave cavity assembly. A photograph of this modified continuous microwave system for laboratory type experiments is shown in Figure 1.

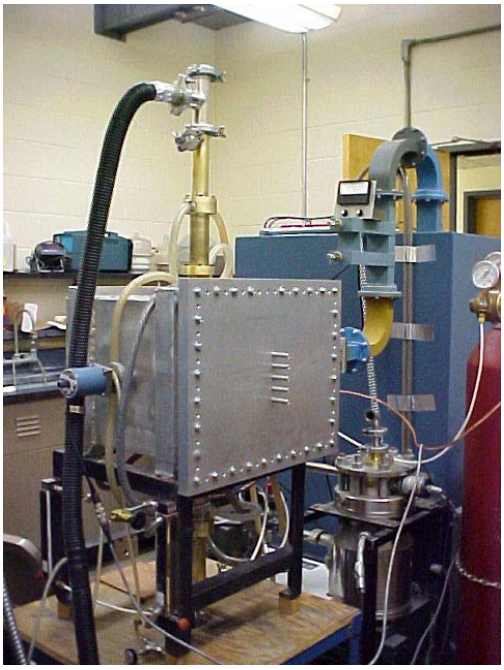

Figure 1. Laboratory Scale Continuous Microwave System modified to sinter Powder Metal Tubular Trial Parts

ii. Continuous Microwave Sintering of Trial Samples: First, in order to develop a continuous microwave sintering of steel samples in the new modified microwave system, trial runs were made with FN208 (Fe:97.2, Ni:2.0,C:0.8) cylindrical samples (1 inch diameter and 1.5 inch height) were loaded in the microwave furnace for vertically continuous sintering. The arrangement is schematically shown in Figure 2. The processing conditions were adjusted to obtain the optimum sintering temperature of 1250°C for processing of FN208 at the center of the cavity. The assembly of the samples was allowed to move vertically downwards with a specific feeding rate. A set of 11 samples was successfully sintered with all samples possessing consistent sinter density. The optimum sintering conditions used were:

Atmosphere: Forming gas (95%N_2+5%H_2), Temperature: 1250°C, Soaking time: 5 min.

Feed rate: 0.2”/min, Total time to sinter 11 samples: 65 min.

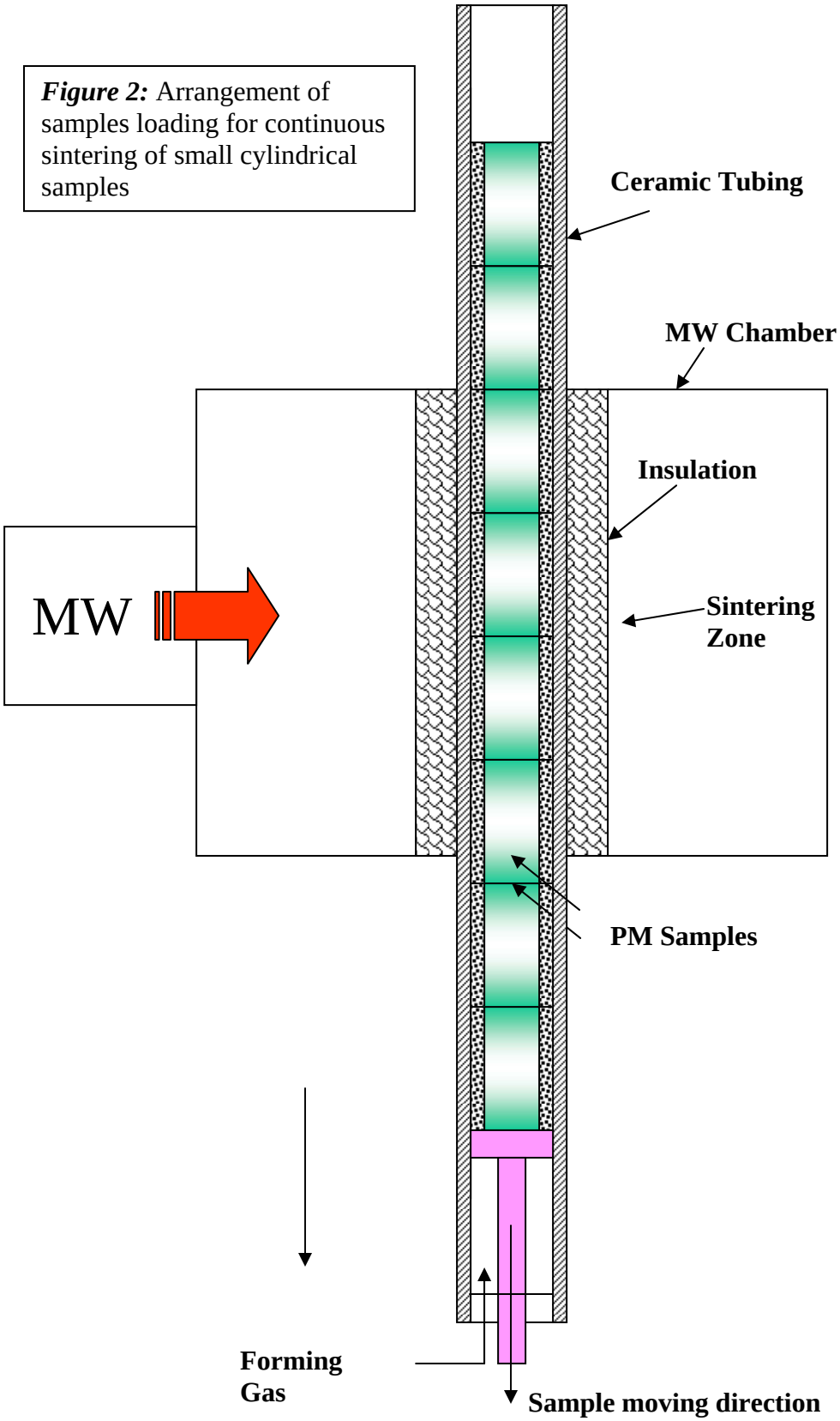

Figure 2: Arrangement of samples loading for continuous sintering of small cylindrical samples

iii. Fabrication of long tubular samples: For fabrication of long tubular specimens both CIP and extrusion methods were adopted.

a. Cold Isostatic Press (CIP): CIP is a standard method for consolidation of powders by pressing uniformly in all directions. In this method uniform pressure in all sides is applied using a wet bag or a dry bag method. For cylindrical specimens an assembly of a rubber bag and a mandrel fixed along the axis is used, providing isostatic conditions. CIP can produce tubular samples up to limited length (30 feet, Loomis Products Company). CIP was used to make 12 inch long solid and hollow tubes of nominally 1 inch OD and 0.75 inch ID. Figure 3 shows CIP equipment available at MRL. It has the capacity of fabricating up to1-inch diameter and 1.5 ft long samples. CIP conditions used in this study were: 30,000 psi for 5 minutes. In order to test the system, trial samples of FC208 steel powder were first made. Having gained enough experience and confidence in CIP process, tubes of the chosen composition of 316 L were made. 15 test samples of about 12 inch in length and 1 inch OD using 316L steel powder mixed with 1.5 wt% binder (Acrawax) were CIP'ed. The binder burnout (removal of Acrawax) of these CIPed samples was successfully done at 450°C in 1 hour. Some samples were also de-waxed *in situ* during the microwave sintering process.

Figure 3. Cold Isostatic Pressing equipment used in this program to make 1" diameter and 12 inch long powder metal tubes

Microwave Sintering of CIP'ed Samples: First trial samples of 12 inch CIP'ed tubes of FC208 as fabricated above were used for continuous sintering. They were sintered to nearly full density at 1200°C with a feeding rate of 0.2 inch/minute. Next some process optimization was conducted on another set of tubes made by CIP. 15 CIP'ed specimens of 316L were used to determine the best microwave sintering conditions in flowing H_2. Some of these samples were sintered in vertical continuous sintering system and some in the newly designed and built horizontal microwave system. After conducting many experiments, optimum sintering conditions were identified and 3-4 good samples were processed for further testing.

b. Extrusion Method: In the extrusion, mixtures of the powders, lubricants, and binders are used, and pushed through cylindrical tooling of desired diameter providing solid/hollow tubular specimens. Extrusion methods can produce virtually any length of tubular objects when the extruder can be continuously supplied with powder mixtures. Two common extruders are used. Screw / auger and piston / ram types are used in powder metallurgy. Both were tested in this study. In the auger type, mixes are fed into the auger and the screw compresses them against and through a die, which shapes the extrudate into the desired shape. This method is easily made into a continuous operation by continuously feeding powders into the hopper of the auger. The disadvantage is that in a continuous operation the maximum pressure applied to the mixtures is relatively low and high binder concentrations are needed to obtain the proper flow through the extruder. In the ram type, high pressures are more easily obtained and binder concentration can be minimized but continuous operation is more difficult since the ram barrel has a finite size and a two barrel switching system needs to be developed in order to have a continuous operation.

In the first year of the program we had conducted extensive extrusion experiments using an in-house Braebender auger extruder. We had developed formulations and non-wax binder powder mixing compositions, and conducted many experiments to identify right amount of the binder and its effect on the viscosity. The details of this work were reported in the Annual Technical report. The extrudate could not be formed into well-shaped rods and this process was abandoned in order to investigate the ram type of extrusion.

A US company, Pennsylvania based Loomis Product Company that has been manufacturing extrusion units and conducts feasibility studies on new powders, was identified and expertise was utilized for this project. We had prepared several batches of 316L powder

mixed with various amounts of Acrawax binder (1.5 to 10 %wt), sent to them for processing green tubes. After a number of attempts to extrude the materials, a 4% binder plus lubricants metal powder mixture was found to be necessary for extrusion. During the last months of the project extrudate of up to four feet long was obtained but the wall strength was not good enough to transport to the MW applicator without damage. Further binder / lubricant work would have to be done in order to obtain strong enough green bodies. The two pieces of equipment have to be brought together before a successful development project could be made.

c. Design and Building of Horizontal continuous sintering microwave Unit: In the Phase I extension program, it was one of the main tasks to build a semi-continuous microwave sintering system with available facilities in our laboratory so that when the extruded tube arrives from Loomis, it could be sintered here rather than sending it to Japan as was originally planned. For this unit we had acquired four 3kW microwave generators, built a microwave cavity capable of processing tubular products in control atmosphere. Figure 4 displays this unit. At present there are couple of problems with the set-up. It has a tendency to create excessive stresses in the casing alumina tube casing during heating and cooling cycle. This often results in breakage of the tube. We are working to resolve this problem for future experiments. However, stainless steel tubes have been well sintered during continuous microwave sintering simulation experiments.

Figure 4. 2.45 GHz, 12 kW (4X3 kW) multi-mode continuous microwave sintering unit for tubulars

4. Results and Discussion

i. Selection, microwave sintering, testing and characterization of test samples:

First several carbon steel compositions that are used by our industrial partner Quality Tubing (QT) for making drill tubing, were selected for microwave sintering investigation. QT receives steel strips from Mitsubishi Metal Work, Japan. The strips are made by melting, casting, rolling, and tempering into thin sheets which are cut to the required sizes. Tubular products are made by folding and seam welding methods. Since these compositions were not available in powder form for Powder Metal (PM) sintering, the current project precursor powders were made by mixing various constituting elements. Usually in PM sintering processes pre-alloyed mixes are used for consolidation. This provides high densification, uniform sintering, and better properties. Since pre-alloyed mixes of QT compositions were not available, non-alloyed pre-mixed powders prepared by Keystone Powder Metal Co. were used for initial studies. *(The details of this study were given in the first Annual report)*

In addition, several steel compositions were discussed with Keystone Powder Metal Company to provide green samples including QT compositions. It was decided that in the beginning for trial runs in our existing vertical microwave system, FN208 and FC208 (Fe:97.2, Ni/Cu:2, C:0.8 wt%), standard steel compositions used for most automotive parts, should be used until new powders were ready for the fabrication of green specimens. The purpose of these experiments was to test our existing microwave system and also to find out if any modifications were needed in the system for sintering of powder metal samples. This system was used for processing powder metal hollow and solid cylindrical samples. 70 green cylindrical hollow and solid samples (about 1-1.5 inch length, 1 inch diameter, and 0.1 inch wall thickness) of FC208 and FN208 were fabricated by cold pressing for trial runs. Some of these samples were processed individually under various temperature and time conditions in flowing forming gas atmosphere (95% N_2 + 5% H_2). The purpose of using forming gas is to provide reducing atmosphere to remove any oxide layer on metal powders and prevent their oxidation. Forming gas is preferred because it is inflammable. After carefully fine-tuning and optimization of the processing conditions, excellent sintered samples of both tubular and solid cylindrical shapes were obtained. Once it was established that in our existing 2.45 GHz, multimode, 6 kW microwave system standard steel powders could be sintered to high density, green pressed samples (solid and

hollow cylinders) of QT900 composition using pre-mixed powders but not pre-alloyed were procured. These samples were microwave sintered between 1200-1250°C for 10 minutes. The samples after microwave sintering under above conditions could not achieve full densification. Since this steel composition was not reported to have sintered via powder metal sintering method, there was no data available on its sinterability. So a systematic study to identify the optimum sintering conditions for QT900 was conducted. For this purpose small discs were fabricated by uni-axial pressing, which were microwave sintered at different temperatures and time conditions under various sintering atmospheres. The goal of this study was to obtain nearly full density with no open or surface porosity. Numerous samples were microwave sintered under varying atmospheric conditions and at different sintering temperatures. The result of this study showed that atmosphere is critical for obtaining good sintering. The best results were obtained with pure or 75% H_2 atmosphere. Still full densification has not been achieved because the elemental powders did not alloy effectively without melting. Therefore, it was decided to look for other steel compositions for further studies.

The pre-alloyed starting powder of Quality Tubing based composition for coiled tubing was not available for sintering purposes. This composition is available only in the form of ingots or flat sheets. The powder of this composition acquired from a powder metal vendor was not pre-alloyed. The pre-alloyed powder for test samples was not possible to obtain in small quantities. And as found above the non-alloyed pre-mixed powder of QT compositions did not result in to good sinterability, a few new pre-alloyed steel compositions which were known to exhibit high strength and high corrosion resistance characteristics, were selected for further investigation. For that reason high chrome based compositions were selected for further studies. After careful examination and preliminary studies of at least four chrome based steel composition 316L was found to be the best and was selected as the final composition for scale-up experiments. Several grades of 316L powders were acquired from various sources and an investigation of sinterability *vs* grain size was carried out. *(For details please refer to first Annual Report)*

As for as particle size of 316L steel powder is concerned, not much difference was found in the sintered density when processed between 1300-1325°C for 15 minutes in pure H_2. Several experiments were performed to sinter 316L under varying processing conditions. These results showed that nearly full density was achieved at 1340°C/10 min. The microstructural data of the above samples are quite consistent with the density results. Typical microstructures of samples

sintered at 1340°C/10 min showed very little porosity, it is just like the microstructure observed in QT900 conventional sample received from Quality Tubing and manufactured from metal strip.

ii. Cold Isostatically Pressed samples sintered in microwave:

After having gained enough experience and confidence in CIP process, tubes of the chosen composition of 316 L were made. 15 test samples of about 12 inch in length and 1 inch OD using 316L steel powder mixed with 1.5 wt% binder (Acrawax) were CIP'ed. For trial runs in the modified microwave system 12 inch CIP'ed tube of FC208 as fabricated above was used for continuous sintering. It was sintered to nearly full density at 1200°C with a feeding rate of 0.2 inch/minute. The sintered samples were cross-sectioned and examined under SEM. Some surface porosity was observed. Surface porosity is defined as the pores developed on the surface of a sintered product, and they are considered undesirable due to the increase in the apparent surface area and thereby making the surface more susceptible to corrosion attacks. Next some process optimization was conducted on another set of tubes made by CIP. After conducting many experiments, temperature of 1250°C and 0.2 inch/min. feeding rate were found to be optimum for FC208.

15 CIP specimens of 316L were used to determine the best microwave sintering conditions in flowing H_2. These samples were successfully sintered in vertical as well as horizontal continuous microwave sintering systems. Figure 5 shows comparison of Yield Strength of microwave sintered 316L and the standard product clearly indicating that microwave sintered product has ~15% higher Yield Strength:

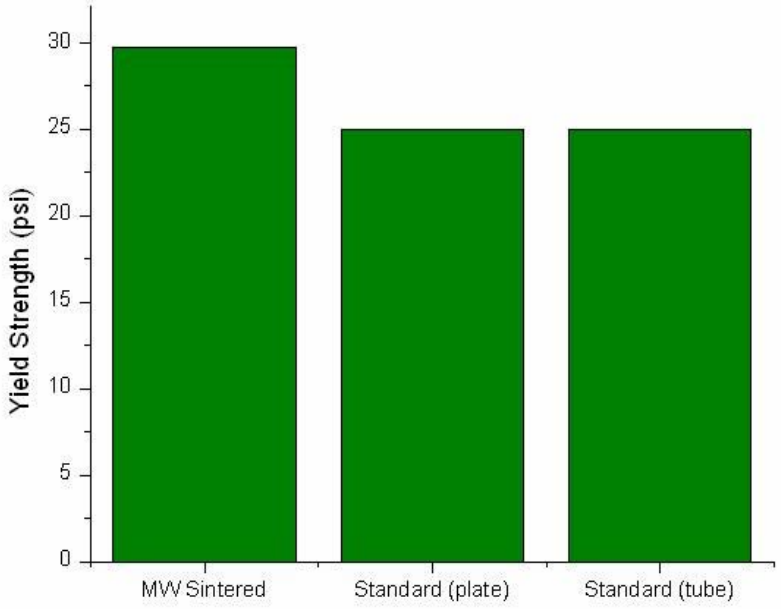

Figure 5. Comparison of Yield Strength of microwave sintered steel tube and standard products

iii. Modification of 316L by adding dopants:

In order to continue to improve the mechanical properties and performance of the chosen 316L steel, a side-study (*at Indian Institute of Technology, Kanpur, India at no cost to the project*) was conducted to modify the composition by adding some oxide dopants to improve the strength and corrosion resistance. For this purpose few % of YAG (Yttrium aluminum garnet, $Y_3Al_5O_{12}$) or Y_2O_3 were added to 316L. These dopants are well known for improving the sinterability and mechanical properties of the steel compositions. The purpose of these two dopants is to eliminate the inter-porosity in 316 L and thereby enhancing the mechanical properties. These samples were sintered by conventional heating method. The microwave sintering experiments have not yet been completed. The conventional data indicating that there was a substantial increase in the mechanical properties of the doped 316L *(details provided in the first annual report).*

iv. Continuous Extrusion Process for Carbon Steel Powders:

In the first year of the program we had conducted extensive extrusion experiments using in-house Braebender extruder. We had developed formulations and non-wax binder powder mixing compositions, and conducted many experiments to identify right amount of the binder and its effect on the viscosity. The details of this work were reported in the Annual Technical report. The extrudate could not be formed into well-shaped rods and this process was abandoned in order to investigate the ram type of extrusion.

As reported in the Annual Report, we had identified a Pennsylvania based US company, Loomis Products Company, which has been manufacturing extrusion units and conducts feasibility studies on new powders. This was very convenient for our project. We prepared several batches of 316L powder mixed with various amounts of Acrawax binder (1.5 to 10 wt%), sent them to Loomis for processing green tubes. After a number of attempts to extrude the materials, a 4% binder plus lubricants metal powder mixture was found to be necessary for extrusion. During the last months of the project extrudate of up to four feet long was obtained but the wall strength was not good enough to transport to the MW applicator without damage.

Recommendations: Originally, it was proposed to accomplish the goals of this program by developing an efficient and economically viable continuous microwave process to sinter continuously formed/extruded steel powder for the manufacture of seamless coiled tubing and other tubular products. However, based on the results and faced with insurmountable difficulties in the extrusion and de-waxing processes, the approach of achieving the goals of the program should be changed. It is recommended that an approach of microwave sintering combined with Cold Isostatic Press (CIP) and joining (by induction or microwave) should be adopted. This process can be developed into a semi-continuous sintering process if the CIP can produce parts fast enough to match the microwave sintering rates.

5. Conclusions

This program has a potential for the development of a novel and innovative technology for the oil and gas industries at a lower cost and better product. The microwave sintering process has been well recognized in academia and industry as faster, better and cheaper. However, until recently these benefits could not be translated into commercial products due to certain limitations of the technology, especially in a scale-up operation. But in the last several years certain developments and successes achieved at Penn State in collaboration with Dennis Tool Company in this field, have taken this technology to the market place, especially in the carbide industry for making carbide inserts and wear parts used in drilling operations for gas and oil exploration. Further, the potential of microwave sintering of metals and steels was unheard of and unthinkable until a few years ago. Now it is a reality that all metals and alloys can be sintered very effectively and efficiently in a microwave field. Our preliminary experiments have clearly demonstrated that microwave produced steel samples have superior mechanical properties than the conventional parts. In case of the drill-pipes, the elimination of the weld seam removes the weakest point in the current system. Leakage and tube fatigue occurs at this point in welded tubing. Also, microwave processing improves the fatigue life and flexibility of the powder metal coils. Fatigue occurs when the coil is rolled and re-rolled multiple times during its use on the drill rig. Higher toughness will allow the tubing to withstand higher internal and external pressures Finally, the microwave processing improves corrosion resistance of materials, and therefore downhole in the hostile corrosive environment microwave processed tubing would last much longer than the current tubing. If the this research program is successfully completed, it will translate into substantial savings in cost and energy for the gas and oil industries.

Microwave/induction joining will produce iso-compositional joints without any stresses in the main body of the tubing because the time of joining is too short and only the braze powder in microwave gets heated, therefore there is no possibility of developing undesired stresses next to the joint location. Further, microwave joining process is faster, effective and economical.