

MANUFACTURE OF PARTICLE REINFORCED STEELS BY SPRAY FORMING

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ABSTRACT

Ceramic powders were added to the metal spray during spray forming of two different steels. For this purpose a specially designed device was used which allows for the controlled injection of powders directly into the atomisation zone. The powders investigated include alumina, silicon carbide and tungsten carbide. The resulting billets were characterised both by micrography, hardness and wear resistance.

INTRODUCTION

Spray forming is a process which allows for preparing metals and alloys with properties such as low oxide content, fine grain size, or a high content of metastable alloy phases. This combination of properties cannot be achieved by conventional casting methods [1]. One feature makes the spray process appear particularly attractive: the possibility for modifying the properties of the sprayed deposit by injecting powders such as oxides, carbides, borides, nitrides or pure metals into the spray cone. The powders are allowed to react with or to be wetted by the liquid metal droplets and to be incorporated into the metal as it is deposited onto the substrate. Metal matrix composites (MMCs) can be made by adding inert powders such as carbides or oxides. Examples of such spray formed MMCs are SiC in aluminium [2], graphite in copper [3], or alumina in steel [3]. When the powders react with the liquid metal to form some product which is then incorporated into the deposit one talks of reactive spray forming. An example for this is the formation of alumina in copper by adding copper oxide to a copper melt containing small amounts of aluminium [3,4]. Moreover, the powders injected may be substances which decompose when they come into contact with the metal and release large amounts of gas. The gas then might generate pores in the deposit. This effect - usually undesired - can help to make highly porous materials for structural or functional applications based on, e.g., copper [5] or steel [6].

For making MMCs large quantities of powder have to be injected into the spray cone to ensure that the final oxide or carbide content in the metal ranges above 20% which is about the minimum content usually needed to achieve attractive mechanical properties of the MMC. For reaction spray forming or for the foam making process, however, lower powder contents can be sufficient. It is crucial that one can disperse the powders uniformly in the metal matrix in order to ensure advantageous mechanical

properties of the resulting MMCs. Much care has therefore been taken to develop an injection device which allows for a reliable distribution of particles.

POWDER INJECTION DEVICE

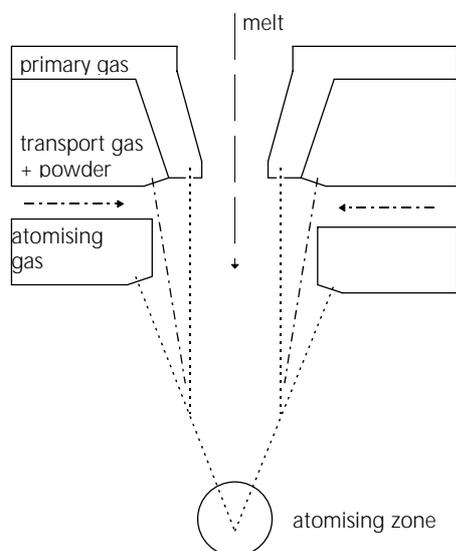


Figure 1: Principle of powder injection used in the experiments

The powder was injected into the spray cone through a specially designed ring of nozzles as described in Ref. [6]. We used a twin screw feeder for transporting the powders from a powder hopper into a mixing chamber. The twin screw feeder was found to transport even damp and partially agglomerating powders in a fairly reliable way without compacting the powders too much. Moreover, the twin screw feeder could be operated at the desired transport rate ranging from 0 and 600 ml per minute. From the mixing chamber the powder was transported to the actual injection nozzle in the spray chamber by a stream of nitrogen gas. In order to ensure good contact between powders and molten metal after injection into the spray cone, a special nozzle for the powder saturated transport gas was installed near the atomisation zone. According to this construction the powder is injected into the region between the atomising gas and the primary gas stream, which stabilises the atomisation process. Figure 1 shows schematically how the various gas jets are oriented. One sees that the powder particles are dragged into the space

between the atomisation stream and the primary gas stream and are directly fed into the atomisation zone this way.

In order to be able to inject more than 600 ml/min of reinforcing particles into the metal spray, the existing device will have to be modified because the cross section of the tubes and nozzles used for powder transport and injection is restricted owing to the very limited space in the atomisation unit.

POWDER INJECTION EXPERIMENTS

Properties of Steels used for the Experiments

Two commercially available steels were used for the experiments: a 0.35% carbon steel (Ck35, SAE 1034) and the stainless chromium steel (X20Cr13, SAE 51420). The carbon steel was chosen because it is an inexpensive material which might have a good application potential as particle reinforced material. The stainless steel is frequently used in machine construction. In the processing of this steel grinding and polishing steps give rise to a large volume of waste material. This waste is collected and could be recycled in the spray forming process thus leading both to an upgrading of the material and to new application fields. The two steels were spray formed according to the parameters given in Table 1.

Steel	Ck35 = SAE 1034	Ck35 = SAE 1034	X20Cr13 = SAE 51420
melting atmosphere	nitrogen	argon	nitrogen
atomisation gas	nitrogen	nitrogen	nitrogen
atomisation pressure	2.5 bar	4 bar	4 bar
distance atomiser/substrate	600 mm	500 mm	500 mm
substrate inclination	30°	30°	30°
excentricity	10	10	10
T_{liq} of metal	1525°C	1525°C	1505°C
superheat	175°C	130°C	130°C

Table 1: Spray parameters for the steels used (old parameter set included for Ck15)

The metal outlet of the tundish had a diameter of 5 mm. With a constant height of the metal column of 250 mm this yielded an average metal flow of 300 g/s. The substrate was rotated at 1.8 Hz and was lowered at a rate of 0.85 mm/s as soon as the deposit reached a height of about 50 mm. First experiments yielded quite porous billets mainly due to cracking in the cooling phase. The reason for this was found to be a too high melt temperature and too low atomisation pressures (first column of Table 1). An adjustment of these parameters (second and third column) lead to macroscopically dense billets. However, some residual porosity could still be found in the microscopic images. The latest experiments were therefore carried out at even lower superheats (120°C) which is actually the limit because an even lower temperature would increase the danger of premature solidification in the metal outlet.

In Figure 2 the pearlitic microstructure of a spray compacted Ck35 (SAE 1034) with injected WC/Ni-88/12 particles can be seen in two magnifications. One can clearly see the remaining porosity near the surface of the billet.

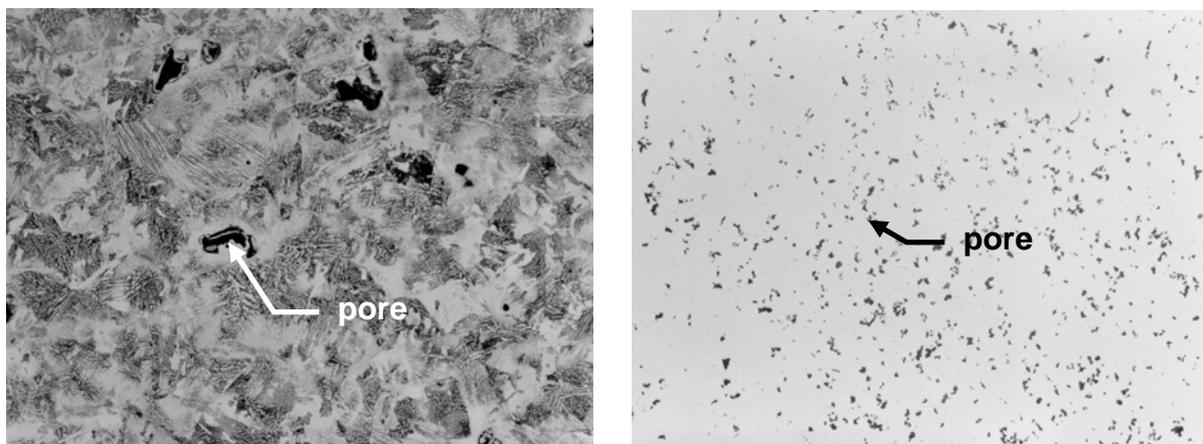


Figure 2: Microstructure of spray compacted Ck35 (SAE 1034) with WC/Ni-88/12 particle inclusions. Left: microstructure near the centre of the billet (etching: pikrin+HCl, field shown is 100×75 µm in size). Right: microstructure of the same billet near the surface (uneched, field shown is 1000×750 µm in size)

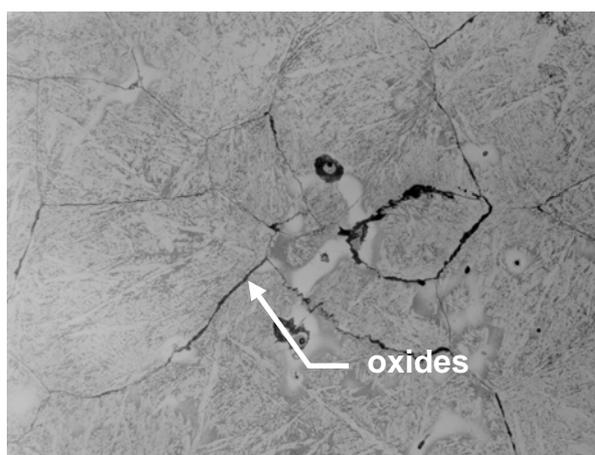


Figure 3: Microstructure of spray formed X20Cr13 (SAE 51420) containing SiC particles and showing oxides along the grain boundaries (etching: pikrin + HCl, field shown is 200x150 µm in size)

The stainless steel shows a notably lower porosity than the carbon steel except for a surface layer of about 10 mm thickness (see Figure 3). What is remarkable are the oxides which can be found on the grain boundaries and which are probably caused by some residual oxygen in the spraying chamber.

Particle Characterisation

Figure 4 shows some of the particles used in the experiments. The corresponding size distributions are given. Obviously, the main fraction of the particles is in the range from 20 to 40 μm . Powders of this size were found to have sufficiently good flow properties for particle injection.

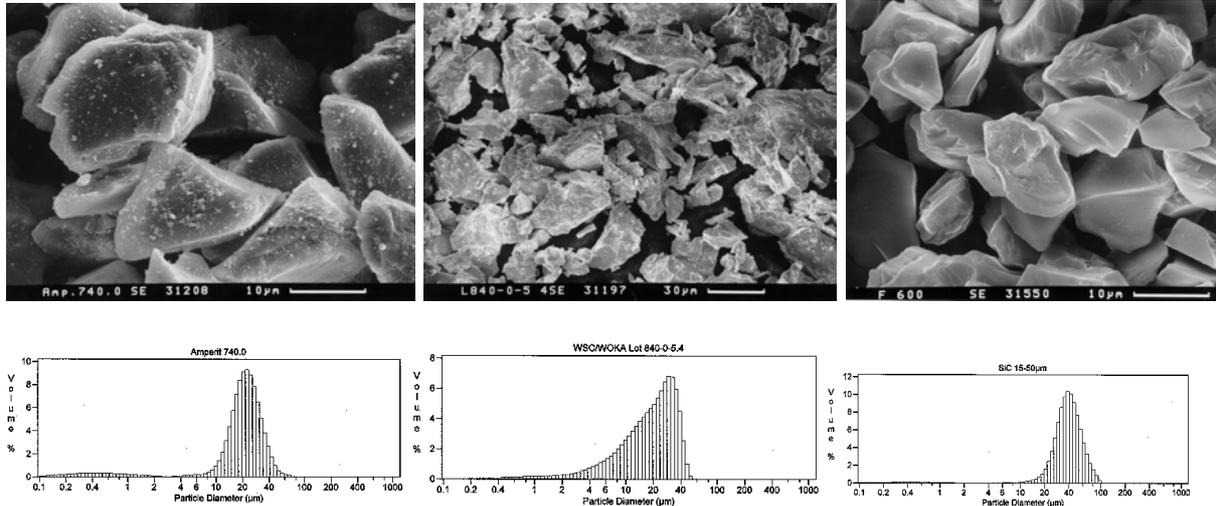


Figure 4: Particle morphology and size distributions of various powders used: Al_2O_3 , WC and SiC (from left to right)

Injection of Alumina (Al_2O_3)

In a first experiment about 2 vol.% Al_2O_3 particles were injected. The resulting microstructure is shown in Figure 5.

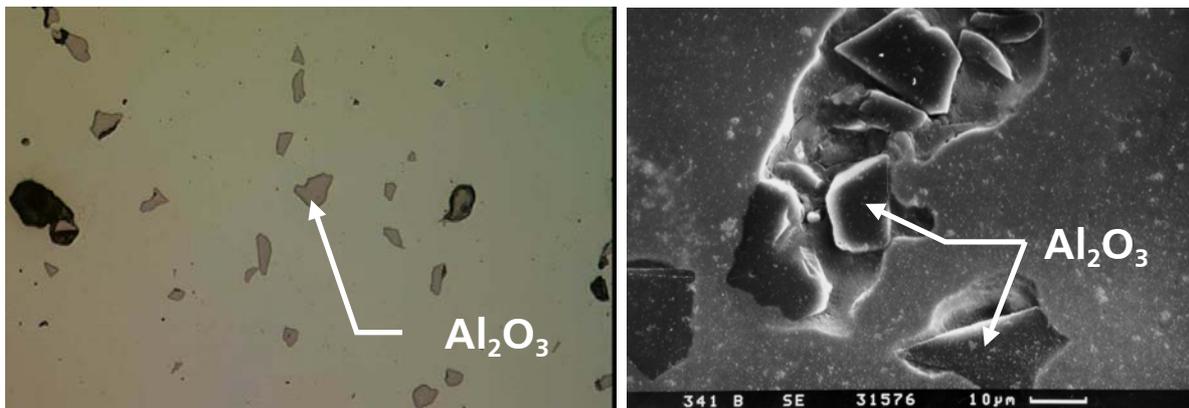


Figure 5: Steel Ck35 with 2 wt.% Al_2O_2 particles. Left: optical micrograph (section shown is 500 μm wide), right SEM image

The alumina particles are obviously enclosed by the surrounding steel but there is no metallurgical bonding between metal and oxide as can be seen in the SEM picture on the right. Sometimes agglomerates of alumina particles can be found.

Injection of Alumina/Titanium Dioxide ($\text{Al}_2\text{O}_3/\text{TiO}_2$)

In a modification of the experiment in the last section the alumina particles were replaced by a mixed oxide of Al and Ti. The embedding of the particles seems to be much better in this case (see Figure 6). Moreover, the particles can be predominantly found in the ferrite surrounding the pearlite grains.

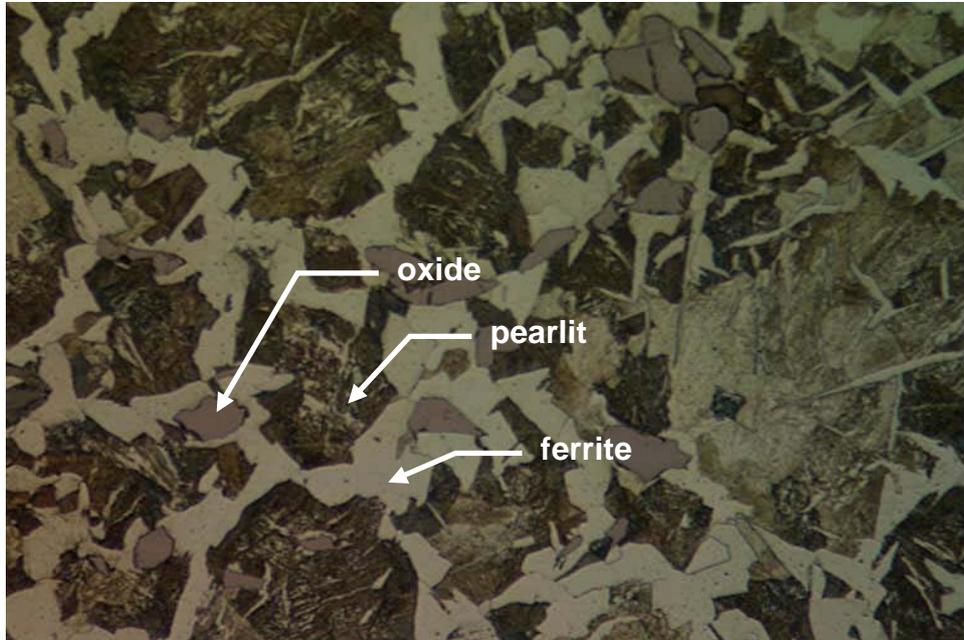


Figure 6: Steel Ck35 with $\text{Al}_2\text{O}_3/\text{TiO}_2$ (3%) particles (section is 500 μm wide).

Injection of Tungsten Carbide (WC) and Tungsten/Nickel (WC/Ni-88/12)

Tungsten carbide powder was injected in a further experiment. Chemical analysis of the resulting deposit revealed a tungsten content of 4 wt.%. The carbide is completely dissolved and not visible any more (see Figure 7). The formation of a very fine and interconnected porosity throughout the sample can be observed.

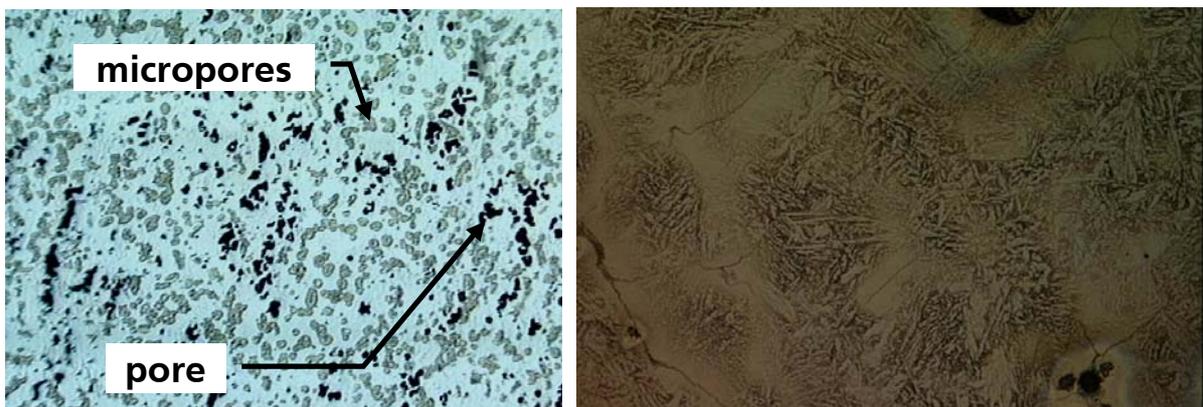


Figure 7: Steel Ck35 after 4 wt.% WC particles had been injected (left: field is 8 mm wide, right: 0.4 mm wide)

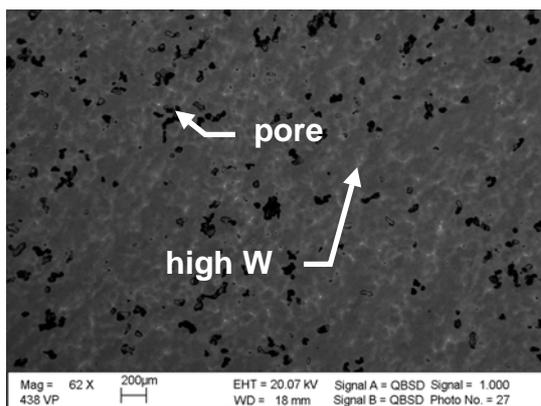


Figure 8: Spray formed Ck35 (SAE 1034) steel with WC/Ni particles after the improvement of process parameters (SEM, backscattering electron mode)

A change of the spray parameters, however, yielded an improved microstructure as can be seen from the SEM picture (Figure 8). This time a tungsten carbide powder with a nickel coating was used to enhance wetting of the particles.

An EDX analysis revealed that the light grey spots in Figure 8 contain 6.8 wt.% tungsten while the dark regions merely contain 1.8 wt.% WC and WC/Ni-88/12 particles are dissolved completely in the steel matrix and can therefore not be seen. Because the cooling of the billet cannot be made very much faster and therefore the dissolution of WC cannot be prevented, the prospects of achieving a particle reinforcements with this additive remain uncertain.

Injection of Silicon Carbide (SiC)

Silicon carbide is an interesting alternative to tungsten carbide because it is even harder than WC and because it is available in many different grain sizes at comparatively low costs. SiC decomposes at high temperatures but the short exposure to heat during spray forming should not lead to its destruction. In first experiments injection of silicon carbide effected in an exothermal reaction in the steel billet. The carbide particles are still visible in the billet and seem to have bonded with the metal (see Figure 9). In a second experiment the reaction was suppressed by choosing a lower melt temperature.

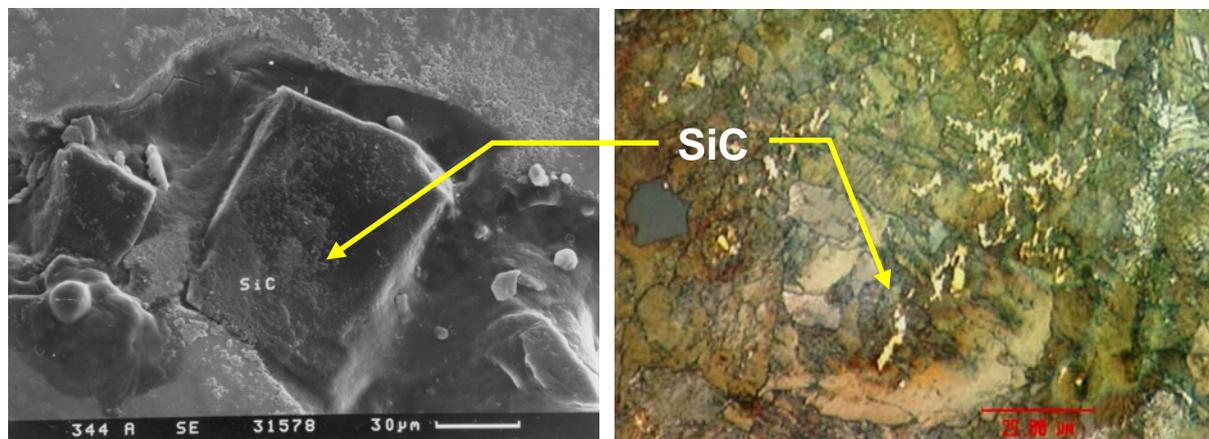


Figure 9: Steel Ck35 after the injection of SiC particles and after an exothermal reaction had taken place (right: field shown is 133 µm wide),

Stainless steels with embedded SiC particles were also manufactured (see Figure 3). As already mentioned, this was unproblematic except for the oxide contamination of the grain boundaries.

MECHANICAL CHARACTERISATION

Hardness measurements

For all samples hardness was measured. Table 2 lists the results:

sample no.	steel	particle	HV30 (average)	scatter
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-	Ck 35 (SAE1034)	none (starting material)	184	0
-	X20Cr13 (SAE 51420)	none (starting material)	256	6
341	Ck 35 (SAE1034)	Al ₂ O ₃	199	n.d.
342	Ck 35 (SAE1034)	WC	309	9
			234	52
343	Ck 35 (SAE1034)	Al ₂ O ₃	217	17
344	Ck 35 (SAE1034)	SiC	240	9
355	Ck 35 (SAE1034)	WC/Ni-88/12	313	48
356	X20Cr13 (SAE 51420)	SiC	328	12
357	X20Cr13 (SAE 51420)	SiC	306	16

Table 2: hardness of various spray formed billets

The macroscopical hardness of the spray formed billets compared to the unsprayed starting material is determined by two factors: the different microstructures and the embedded particles. Because the particle content is quite low the influence of the former factor is probably predominant. Hardness can vary between different regions of the billets. The stainless steel, e.g., showed hardness values between HRC 30 and 50. The reason for this is not quite clear. One could speculate that for the carbon steel hardness is increased in regions where WC has been dissolved, whereas for the stainless steel an influence of different thermal history of the various parts of the billets (temperature heterogeneities during spraying and exposure to heat during cutting of the samples) seems possible. Even different billets of the same material show different hardness values owing to slightly different spraying parameters. The stainless steel showed higher hardness values in the sprayed state as compared with the state before spraying although a non negligible microporosity is given. This resulted in a quite difficult machinability of the billets.

Characterisation of wear

For a further mechanical characterisation the wear resistance of the sprayed and - as a reference test - of the starting materials was determined. Pin-on-disk tests were carried out for 4 different samples. For this pins with 8 mm diameter and 15 mm length were cut out of the billets. The disk was a bearing steel (100Cr6 wit 1% C and 1.5% Cr) with a hardness of HRC62. The testing load was 0.75 MPa and an emulsion of alumina and water was used as lubricant. The experiments were stopped after a run of 5440 metres except for the stainless steel starting material which had to be stopped after 2240 m owing to strong wear.

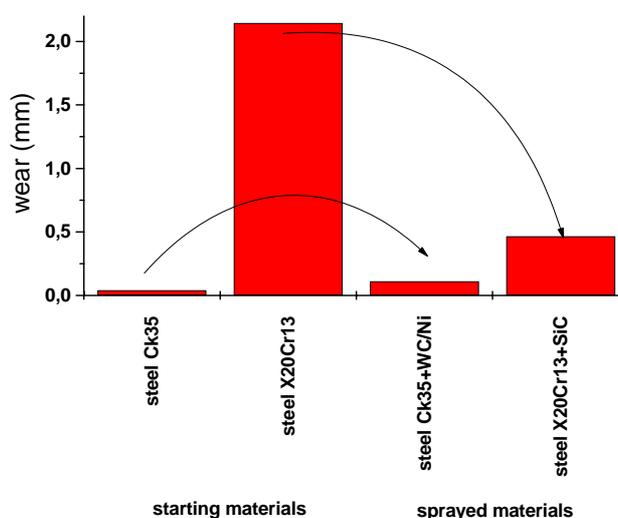


Figure 10: Wear tests on untreated steels and spray formed reinforced steels.

The carbon steel Ck35 (SAE 1034) showed a comparatively low wear under the conditions chosen, whereas wear of the stainless steel X20Cr13 (SAE 51420) was so high that the test had to be stopped. The friction coefficient increased from 0.3 to 0.5 for Ck35 and fluctuated between 0.3 and 0.9 for X20Cr13. The corresponding Ck35-billets with particle inclusions showed a slightly higher wear reflecting that the hardness increasing effect of the particles is overcompensated by the increased porosity level. In contrast spray forming dramatically increased the wear resistance of the stainless steel. The hardness increase during spray forming and the associated particle incorporation produce this increase by a factor of 10 (corrected for different test lengths).

SUMMARY

It was shown that particles can be incorporated into unalloyed and stainless steels in low volume fractions during spray forming. The distribution of particles was fairly uniform and in some cases a bond was observed between particles and steel. At the present state of the still ongoing studies the most promising particles seems to be silicon carbide. In combination with stainless steel a strong increase of hardness and wear resistance was observed even for the low particle contents achieved. Future investigations include injecting higher amounts of particles into the melt and different particle sizes.

ACKNOWLEDGEMENT

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