Manufacture of Novel Composites by Spray Forming

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Abstract

Silicon carbide, *alumina and tungsten carbide powders* were *added* to *the metal spray during* sprayforming of *two different steels. For* this purpose, a *specially designed* device was used which *allows for the controlled* injection ofpowder *particles directly* into the *atomization zone where they mix* with *the* metal droplets *After deposition, the resulting billets* were *characterized* both *by micrography, hardness measurements* und *wear resistance tests.*

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 caniiot he achieved hy conventional casting methods[1,2]. One feature makes the spray process appear particularly attractive: the possihility for modifying the properties of the sprayed deposit by injecting powders such as oxides, carbides, boiides, nitridcs or pure metals into tlie spray cone. The powdcrs 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. Known examples of such spray formed MMCs arc SiC, Al_2O_3 or C (graphite) in aluminum[3,4], SiC in magnesium[5], graphite in copper[5], or alumina in steel[6]. Besides, by this so-called inert spray forming "MMCs can be made by reactive spray forming, where the reinforcing particlcs are formed during spraying by gas-liquid, liquid-liquid or solid-liquid reactions of the metal and the atomizing atmosphere and/or additions to the melt[7-10]. Reactive spray forming enahles one to crcate subniicrometer sized inclusions for dispersion strengthening, whereas the inert spraying process used in the present work rather aims on coarser particles ranging from 3 to 50 µm.

For making MMCs one has to be able to disperse ceramic powders uniformly in the metal matrix and to ensure a good contact hetween particles and liquid metal during the deposition process therefore achieving sufficient wctting of theparticles hy the metal. Much care has therefore bcen taken to develop an injection device which allows for an effective and reliable distribution of particles[10].

This paper reports on tlic injection of silicon carbide, alumina and tungsten carbide into two different stcels. The resulting microstructure aiid some mechanical properties are discussed.

Experimental Procedure

The powder was injected into the spray cone using a specially designcd injection system[10]. Such devices are not new hut only sparse descriptions exist in the literature[3,12].

A twin screw feeder was used for transporting the powders from a powder hopper into a mixing chamber at rates between *0* and *600* ml per minute (see l.h.s. of Figure 1). The powder transport gas which is applied to the main transport line with pressures up to *2.5* hargoes through a nozzle and creates a suction which drags the powder from tlic mixing chamber into the line. From there it is transported to the actual injection nozzle in tlie spray chamher. The atomizing system consists of three rings of nozzles which create three concentric, conical shaped gas jets as depicted in (Figure 1) (r.h.s.). The powder goes through the ring in the middle and is therefore injected into the region between the atomizing gas nnd tlic primary gas stream, which stabilizes the atomization process. This way tlic powder particles cannot escape and are guided into thc atomization zone. This way a very intense contact between the ceramic particles and the metal droplets is ensurcd.

In a first series of experiments the two steels were spray formed by using "standard parameters established for spraying without particle injection: in thcsc tests the metal outlet of the tundish had a diameter of 5 mm. With a con-

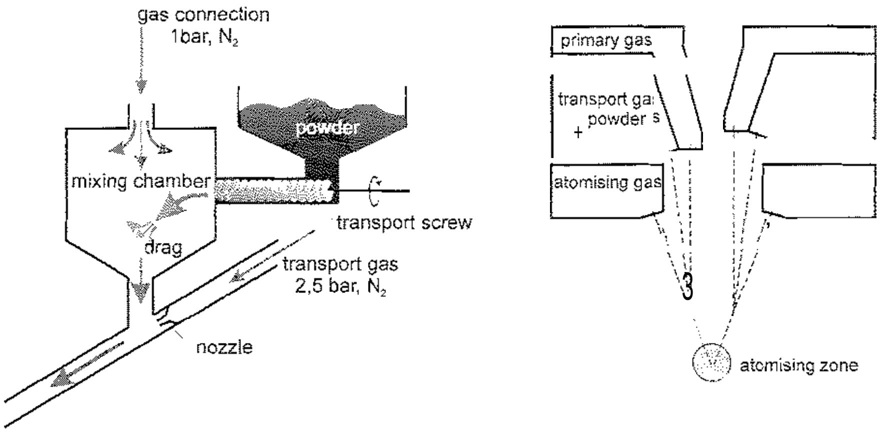

Figure 1. Device for injecting powder into the spray cone. Left: Powder transport unit, right: arrangement of a various gas jets.

stant height of the metal column of 250 mm this yielded an average metal flow of 300 g/s. The substrate was rotatid at 1.8 Hz at a distance to the atomizer of 500 mm and was lowered at arate of 0.85 mm/s as soon at thc deposit reached a height of about 50 mm. The first experiments yielded quite porous billets mainly due to cracking in tlie cooling phasc. Moreover, in thc case of silicon carhide strong metallurgical reactions between thc SiC particles and one of the steels (C35) could be observed. The reasons for this were thought to bc a too high melt temperature and too low atomization pressures. An adjustment of spraying parameters, namely a reduction of tlie melt temperature and the distance between atomizer and substrate and an increase of tlie atomizing gas pressure lead to macroscopically denser billets in subsequent series of experiments. However, as some residual porosity could still be found in thc microscopic images, the latest experiments with SiC and C35 steel were carried out at even lower superhents (120°C) uhich is actually rhe limit because an even lower temperature would increase the danger of premature solidification in the metal outlet.

Materials

Steels

Two commercially available steels wcrc used for the experiments: an unalloyed steel containing 0.35% carbon (German dcsignation: C35, USA: SAE 1034) and a ferritic stainless steel containing 0.2% carbon and 13% chromium (German designation: X20Cr13, USA: SAE 51420). The first steel was chosen because it is a widely used and inexpensive material which might have a good application potential as particle reinforced material. The stainless steel is frequently used in machine construction where its processing. e.g. by grinding and polishing, gives 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.

Powders

Alumina (Al_2O_3) is inexpensive and available in many grain sizes. Five different powdzrs were obtained with mean particle disnieters ranging from 10 to 110 µm. The powdrrs were characterized by means of microscopy aiid by technological powder flow tests such as the measurement of the angle ufrsposc. The powder with the best flow properties had a mean dianieter of 22 µm diameter and was selected for the spray forming experiment, Table 1. This powder is frequently used in plasma spraying and is a standard commercial product. A similar powder containing 3% titanium oxide was also considered. Such mixed oxidcs are used, e.g., to make plasma sprayed coatings in textile industry.

Next, various different tungsten carbide baszd powders were considered. The two powders which were found to be suited for transportation in our injection system included a 20µm R'C powder which is normally usad as filler metal in welding and a tungsten carbidc powder with a protective nickel coating.

Silicon carbidc is an interesting alternative to other common ceramics such as tniigsten carbide because it is even harder than WC and because it is available in many different grain sizes at comparatively low cosis. SiC is dissolved in liquid steel at high temperatures but the

Table 1. Ceramic Powders used for the Spray Fonning Experiments.

particle	manu-facturer	type	powder size [µm] range givnn by manufacturer	own measurement	d_{50}
Al_2O_3	HC Starck	Amperit 740.0	5.6 - 22.5	5 - 45	22
$Al_2O_3 + TiO_2$	HC Starck	Amperit 742.0	5.6 - 22.5		
WC	WOKA	WOKA WC	5	10 - 90	20
WC + Ni	WOKA	WOKA 8812-Ni	29 - 53	2 - 45	43
SiC	Norton	F 320	15 - 50	12 - 30	41

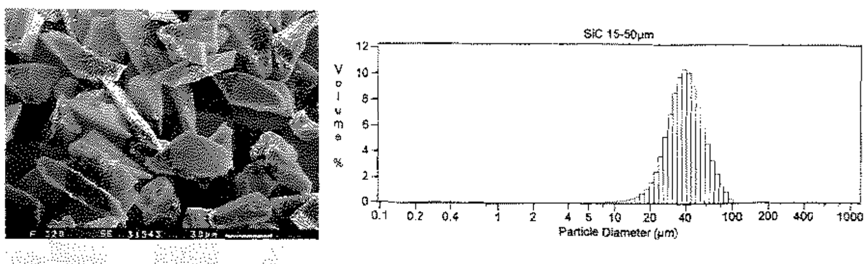

Figure 2. Particle morpholcgy and size distributions of the SiC powder used.

short exposure to heat during spray forming should not affect it too much. Again, SiC powders of various sizes were taken into consideration. Figure 2 shows a micrograph and a particle size distribution of thc SiC particles used in tlic experiments. Obviously, the main fractinii ofthe angular-shapcd particles is aboiit 40 µm in size. This powder is used in grinding industry and is fairly inexpensive.

Microstructures

Al_2O_3 + C35 Steel

Alumina particles were injected into a steel C35 spray at various rates ranging up to 700 g/minute. Tlie highest rate corresponded to an addition of 1810 g of ceramic powder while at the same time 35 hg of steel were atomized.

A resulting microstructure is shown in (Figure 3) (l.h.s.). One sees a fairly uniform distribution of particles and a few residual pores (appearing slightly darker than tlie particles). The volume fraction of particles was determined by quantitative image analysis of a polishcd sample and was found to be 3.5% in tlie case shown. The global contcnt of particles in a spray foniicd billet is difficult to determine because local contents obtained from micrographs cannot be easily extrapolated to the entire sample owing to inhomogeneities of thc distribution. Tlie dciisity of the sample corresponded to about 99% of the theoretical dcnsity if one assumes a particle content of 3.5% As the porosity level appears to be substantially lowerihan 1% from (Figure 3). there either must be some porosity in regions ufthe sample not visible here or the theoretical full density is overestimated. The mass ratio of injected particles to the total sprayed metal is 1:19, corresponding to a volume ratio of 1:9. One would therefore expect a particle fraction of 11% instead of merely 3.5%. The discrepancy is a manifestation of the higher particle overspray for ceramic particles as compared to steel droplets arising from the difference iii density of steel (7.8 g/cm^3) and alumina (3.8 g/cm^3). Lighter alumina particles are more proiie to hydrodynamic drag which removes them from the spray cone more easily than the heavier steel particles.

Figure 3 (r.h.s.) also shows an embedded powder particle in more detail. One sees the ferritic (light) and pearlitic (dark) phases of the steel and the embedded particle (black). All particles are surrounded by ferrite. This means that the hard alumina particles reinforce the softer and more ductile phase ofthe steel which could be iinportant for applications.

The mixed oxide Al_2O_3+3%TiO_2 behaved very much like pure alumina.

Al_2O_3 + X20Cr13 Steel

Tlic same aluinina powder which was injected into C35 steel was also used for reinforcing rhe ferritic steel X20Cr13 in spray forming experiments. Up to 1200 g/minute were added, corresponding to an amount of 3050 g in 35 kgofstcel. One resulting microstructure is given in (Figure 4).

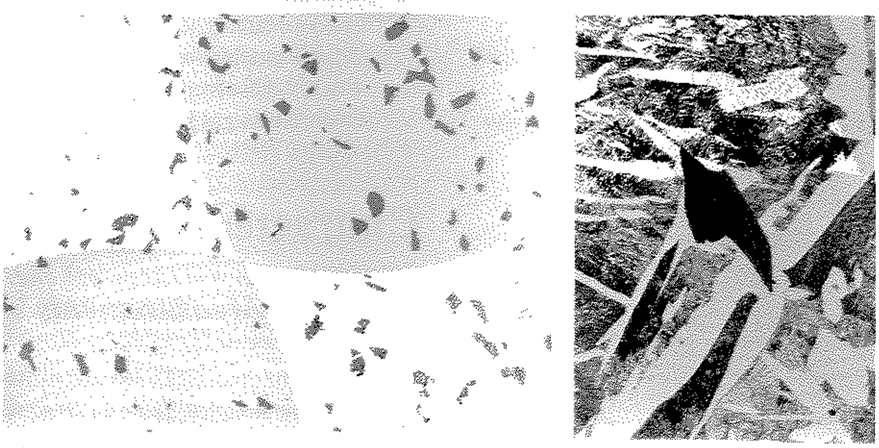

Figure 3. Al_2O_3 particles embedded in spray formed C35 steel. Left: only polished, right: etched in pikrin acid – HCl.

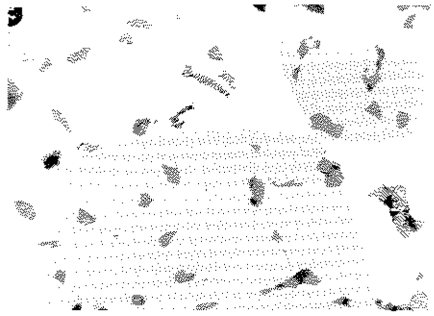

Figure 4. Al_2O_3 particles embedded in spray formed X20Cr13 steel.

One sees that a uniform particle disrnbution and a low content of residual pores (darker patches in Figure 4) could be achieved. The volume fraction is slightly higher than in the materials shownin (Figure 3). However. such good microstructures were limited to the centre of the sprayed billets. In tlie outer regions the content of residual porosity was significantly higher. Although parameter variations were not carried out to an optimum, it seems that one can conclude that the ferritic steel is more prone to porosity foimation in the presence of ceramic particles than the C35 steel.

SiC + C35 Steel

In first experiments tlie injection of silicon carbide caused an exothennal reaction in the C35 steel. However, the carbide particles are still visible in the billet and have even bonded with the metal. The example shownin (Figure 5) demonstrates this nicely. Note that in injecting silicon carbide into tlic ferritic steel no metallurgical reactions of this hiiid were observed.

In a second experiment tlic reaction was suppressed by choosing a lower melt temperature. This lead to an improved macrostructure with still a good bonding between steel and SiC.

Spray forming experiments with various injection rates of SiC were carried out. Tlic highest powder injection rate applied was about 600g/min corresponding to 1.6 kg powder in 35 kg steel. This mass ratio of 1:21 corresponds to a volume ratio of about 1:8. The situation is therefore tlie same as for Al_2O_3 iii C35: instead of a volume content of 12.5% one merely finds aboiit 4% owing to rhe much larger ovcrspray for ceramic particles.

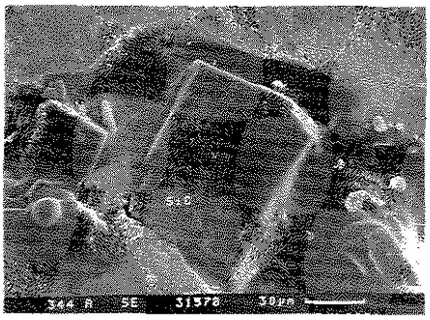

Figure 5. Steel C35 with embedded SiC particles.

The resulting microstructure of one such C35 steel with embedded SiC particles is shown in (Figure 6). The SiC particles are needle-shaped and show a tendency to agglomerate in small clusters. Some residual pores can also be seen.

WC in C35 Steel

Tungsten carhide powder was injectedinto C35 steel in further expeiirnents. Chemical analysis of the resulting materials revealed a tungsten content of 4 wt.%. The carhide, however, was completely dissolved and not visible any more. Nickel coated tungsten carhide powders lead to similar results. The dissolution of particles could not he prevented[11].

Discussion: Porosity

The formation of porosity is always a problem when spray forming metals by choosing appropriate process parameters, by using heated substrates etc. one can minimize such effects". The problem is exacerbated by the presence of ceramic particles in ths steel spray. Initially, the additional cold powder changes the thermal conditions. If the spray parameters are left at the values determined for particle free steels, the result will he a roo cold spray with the usual consequences. Secondly, ceramic particles niight act a Separators between individual steel droplets and prevent them from properly amalgamating to a metallically honded bulk.

In the present studies the residual porosity could not he lowered helow ahout 1% by appropriate Parameter adaptions which is more than for particle free spraying and quite some residual porosity could he found even in the best samples.

Although porositv is an unwanted phenomenon, it is instructive to study the forms of porosity which occur. Figure 7 shows one type of porosity which occurs when the temperature ofthe impactingmetal droplets is too low, e.g., because standard parameters were used which did not take account of the additional particles acting as a heat sink. In this case the impacting metal droplets solidified very quicklv As the spray cone scans over the revolving substrate, the metal is deposited discontinuously. After each revolution liquid metal hits an already solidified surface thus giving rise to typical cold porosity. As a result a staircase-shaped layer of pores is fonned. This cold porosity can he rcmoved. e.g., hy increasing thc thermal content of the spray[13].

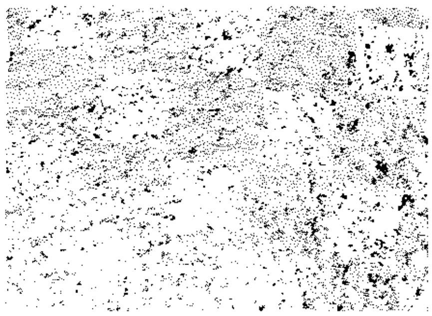

Figure 7. Cold porosity in a X20Cr13 steel to which alumina particles were added

Figure 8 shows a region with pronounced porosity in a highcr magnificatioii. The grey alumina particles stand in contrast with the light stccl matrix and the dark pores. It is apparent that thc particles accumulate preferentially on the inner walls of the pores. Hardly any particles can hc found which are completely enibedded in the steel matrix in this cnse. This is observed in deposits which show cold porosity as well as in ones which have developed more rounded gas pores.

Various possible explanations can he given for this observation, namely:

i) as already described thc cold ceramic particles disturh thc compaction process hy causing premature solidification of the metal droplets and therefore creating cold porosity,
ii) the ceramic particles are incorporated into the liuuid metal hut then float towards the next oore duc to in sufficient wetting, thus minimizing their surface energy;
iii) particles which are tmpped in thc liquid metal might act as heterogeneous nucleation centers for gas whicli is dissolved in the melt and which forms gas pores next to the particle.

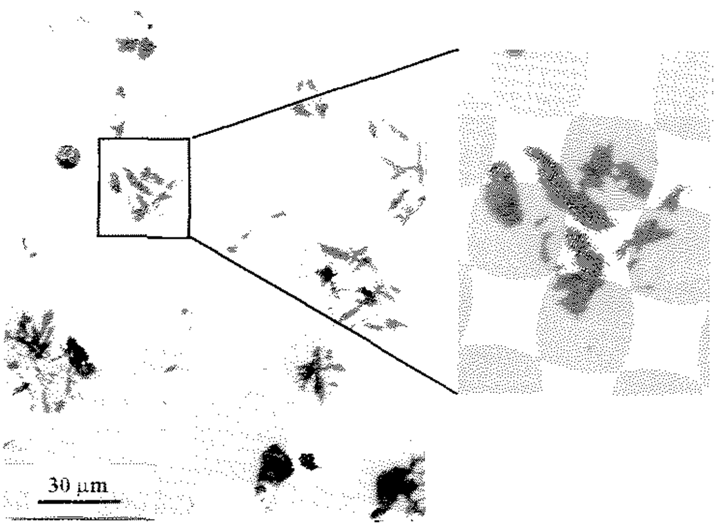

Figure 6. SiC particles embedded in spray formed C35 steel (volume content about 4%).

Characterization

Hardness Measurements

Vickers hardness (HV30) was measured for all the samples. Table 2 lists some of the results. Nine values were obtained for each sample from which an average

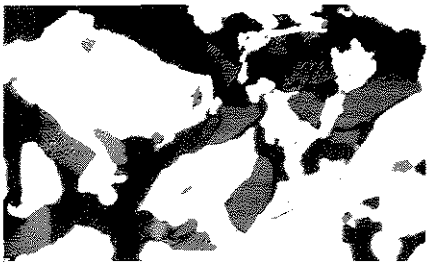

Figure 8. Al_2O_3 particles embedded in a porous region of C35 steel.

was calculated. One sees that in all cases rhe averaged hardness is higher in the sprayed state as compared to the iiisprayed starting material. Hoxcver, it is also obvious that the scatier is very large for some of the samples.

The macroscopical hardness of spray formed billets compared to unsprayed starting matenals is expected to be influenced by various factors:

i) by tlie specific microstructure of the sprayed steels,
ii) by the porosity of the billets, and finally,
iii) by the embedded pariicles.

That the former infliience can be quite important can be seen by looking at billets with low particle conteiit aiid low porosity. Even for such sainples tlie hardness varied considerably between different regions of the sample. One sample made of the stainless steel. e.g., showed hardness values between HV 300 and 550. This observation can probably be explained by different thermal Iiistories of various paris of thc billets (temperature heterngeneities during spraying and eveii cxposure to heat during cultiiig of the samples). Even different billets of the same material show different hardness values owing to slightly different spraying parameters, Table 2, where two values are given for each MMC.

Pores in the materials lead to an unpredictable influence on Iiardness. A hidden pore near the location where hardness is measured can produce unrealistically low values. On the other hand, an accidental particle agglomerate near the location of the hardness measurement will yield a too high value.

In conclusion. the influence of the embedded particles on hardness is difficult to separate from the nther factors. The values listed in Table 2 suggest that there is such an influence but definite values cannot be given. It was thzrsfore concluded that hardness is not a sufficiently suited quantity to characterize MMCs.

Characterization of Wear

For a further mechanical characterization the wear resistance of the sprayed and - as a reference test - of tlie starting materials was determined. For this, pin-on-disk tests were carried out on different samples. Two tests were conducted for each material. Pins with 8 mm diameter and 15 mm length were cut out ofthe billets. The disk was a bearing steel (100Cr6 with 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 meters except for thc stainless steel starting material which had to be stopped after 2240 in owing to strong wear.

The unalloyed steel C35 (SAE 1034) in its untrcated state showed a comparatively low wear under the conditions chosen, whcrens wear of tlic stainless steel X20Cr13 (SAE 51420) was so high that the test had to be stopped. Tlie friction coefficient gradually increased from 0.3 to 0.5 for C35 while it fluctuated between 0.3 and 0.9 for X20Cr13. Spray formed C35 billets without particles showed a slightly incrcased wear, most probably due to soinc porosity. For X20Cr13 spray forming alone already rcduccd wear by about 50%. Here it can be assumed that the microstructural changes in the material due to spray forming overcompensate the presence of some pores.

Particle inclusions in the C35 steel produced a decrease in wear resistance in the first test series. Tlie reason for this rather disappointing result was quickly identified: Due to non-optimised spray parameters tlie porosity was rather high. A second series of spray experiments then produced MMCs with an improved density (such as the ones shown in Figures 3, 4 and 6) which also had improved wear propertics. In rhs best case an increase by a factor of 10 compared to the particle-free but sprayed state could be realized. SiC aiid alumina additions to X20Cr13 had asimilar effect: incriases of wear by factors of 2 and 6, respectively, could be achieved.

In conclusion there is no doubt that wear resistance of steels can be enhanced by adding ceramic powders to the steel during spray forming. The exact relationship between wear and particle type and content, however, still has to be determined.

Summary

It was shown that ceramic powders such as silicon carbide, tungsten carbide and alumina can be incorporated into unalloyed and stainless steels in volume fractions up to about 6% during spray forming. The distribution of particles was fairly uniform and in some cases a chemical bond between particles and steel was

Table 2. Hardness of Various Spray Formed Billets.

steel Germany	steel USA	particle type	HV30 (average)
C35	SAE1034	none	184
		Al_2O_3	199
			217 ± 17
		WC	309 ± 9
			234 ± 52
		WC / Ni	313 ± 48
		SiC	240 ± 9
			324 ± 40
X20Cr13	SAE 51420	none	256 ± 6
		SiC	328 ± 12
			306 ± 16

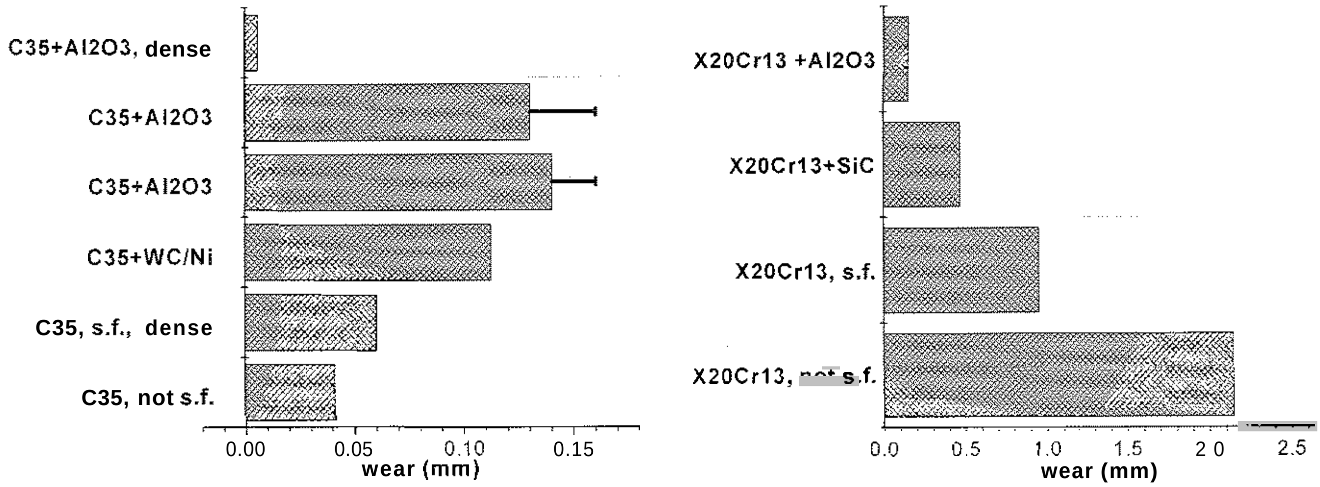

Figure 9. Wear tests on untreated, spray formed and particle-reinforced reinforced steels.

observed. Only silicon carbide and alumina remained in the melt as particles, whereas tungsten carbide was dissolved. Particle reinforced steels were found to have improved wear properiies provided that they were virtually pore free. What remains to be shown in the ongoing work is the relation between particle content and particleisteel bonding conditions on one side and wear aiid other mechanical properties on the other. Moreover, even highcr contents of particles will be considered. Porosity could not be completely eliminated in all the experiments. Probably a mechanical post-treatment, e.g. hy rolling. is necessary to obtain completely dense products and therefore the hest mechanical properties.

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