

THERMODYNAMIC AND EXPERIMENTAL STUDY OF ROLE OF TEMPERATURE AND GRAPHITE ADDITIONS ON OXIDE REDUCTION DURING SINTERING ASTALOY CRL

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TERMODYNAMICKÉ A EXPERIMENTÁLNE ŠTÚDIUM VPLYVU TEPLOTY A GRAFITU NA REDUKCIU OXIDOV PRI SPEKANÍ ASTALOY CRL

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Abstrakt

Chróm, ferit stabilizujúci prvok, zvyšujúci prekaliteľnosť a pevnosť spekaných ocelí je v tradičnej tavnej metalurgii často používanou legúrou [1]. Jeho široké využitie v práškovej metalurgii (PM) bolo donedávna limitované. Dôvodom je vysoká afinita chrómu ku kyslíku a tvorba termodynamicky stabilných oxidov. Oxidické častice na povrchu častíc prášku negatívne vplyvajú na tvorbu medzičasticových spojení, dôsledkom čoho dochádza ku degradácii konečných mechanických vlastností spekaných súčiastok. Nevyhnutnou podmienkou tvorby kvalitných medzičasticových spojení, bez prítomnosti oxidických fáz, je redukcia oxidických častíc a zabezpečenie redukčných podmienok počas celého cyklu spekania.

Podľa [2,3] je redukcia oxidov počas spekania chrómom legovaných ocelí výsledkom kombinácie redukčného potenciálu spekacej atmosféry a uhlíka prítomného vo forme grafitu.

Príspevok sa zaoberá redukciou oxidických častíc predlegovaného, vodou rozstrekovaného oceľového prášku Astaloy CrL, nominálneho zloženia Fe-1.5%Cr-0.2%Mo. Na základe termodynamických výpočtov podľa Mitchella [3] bola určená požadovaná skladba spekacej atmosféry pre redukčné spekanie Fe-Cr-C systému v atmosfére zmesi dusíka/vodíka.

Bola sledovaná redukcia oxidických častíc po spekaní pri teplotách 1120°C a 1200°C bez a za prítomnosti uhlíka v atmosfére 10% H_2 /90% N_2 . Morfológia, distribúcia a zloženie oxidických častíc na časticiach východiskového prášku, a po spekaní prášku a práškovej zmesi bola sledovaná na pričnom reze častíc prášku pomocou LOM, SEM a EDX analýzy.

Abstract

In conventional metallurgy, chromium is commonly used as an alloying element. It is a ferrite stabilizer and a carbide former, and it also improves hardenability [1]. However, its use has so far been rather limited within the powder metallurgy (PM). This element has high oxygen affinity and tends to form thermodynamically stable oxides. Oxides present on the powder particles play an important role in the sintering process since they may inhibit the formation of metallic bonding between the particles. Consequently, the mechanical properties of sintered compounds are affected. For sintering of steels alloyed elements with high oxygen affinity

protective atmosphere of special compositions is required. It was established [2, 3] that oxide reduction during sintering of Cr alloyed steels is the result of combined action of admixed carbon and the oxygen potential of sintering atmosphere.

The present article deals with reduction of oxides particles of pre-alloyed water atomized powder Astaloy CrL with the nominal composition of Fe - 1.5wt%Cr - 0.2wt %Mo.

According to Mitchell [3] theoretical thermodynamic calculation of required atmosphere composition during the sintering of Fe-Cr-C system in nitrogen/hydrogen atmosphere was carried out, paying special attention to carbothermal reduction process.

The reduction of oxide with and without admixed graphite addition was studied after sintering at 1120°C and 1200°C. The morphology, distribution and composition of oxide of powder particles as a received powder as well as powder particles after sintering in atmosphere of 10%H₂/90%N₂ has been studied on cross sections of particles under the LOM, SEM and EDX analyses.

Keywords: chromium alloyed steel, surface and internal oxides, carbothermal reduction, sintering

1. Introduction

Powder metallurgy is a well established manufacturing process for production of iron based and steel components with a diversity of geometries and closed dimensional tolerances for automotive industry and other engineering applications.

Copper, phosphorus, nickel and molybdenum (elements with relatively low oxygen affinity) [4] have been traditionally used as alloying elements in PM, besides the necessary carbon added as admixed graphite. These classical PM alloy steels are easily sintered in atmospheres with moderate dew points. Today's actual trends of PM are associated with modern powder grades with Cr, Mn, Si and V as alloying elements. Chromium as an alloy element is widely used in structural and tool steels produced by ingot metallurgy. However the use of Cr has been rather limited within PM industry due to high oxygen affinity so far. The thermodynamic stability of Cr oxides is significantly higher than oxides of Fe, Ni, Cu or Mo. This means that the compacts have to be sintered in atmospheres with low oxygen partial pressure [4, 5].

Karlsson [6] reported that Cr alloyed powders are covered with particulates of Si-Cr-Mn-rich oxides of size ranging up to 100 nm and thin Fe - rich oxide layer of about 7 nm thicknesses in average. Besides this, surface oxides, the powder particles contain a high amount of internal oxides [2]. The internal oxides are spherical (10-200nm) and are Cr rich for the M₂O₃ type.

Oxides present on the powder surfaces play an important role in the sintering process since they may inhibit formation of metallic bonding between the particles [7, 8].

These facts may have an impact on mechanical and chemical properties of the final sintered products.

Sintering of steels alloyed by elements with high oxygen affinity requires protective atmospheres of special composition. Sintering atmospheres have to reduce residual surface oxides, to avoid re-oxidation and prevent carburization/decarburization during sintering. For proper control of a sintering atmosphere the understanding of the interaction between the green part and the atmosphere is a necessity.

2. Experimental procedure

The experimental powder used in this experiment was prealloyed water atomized powder Astaloy CrL with the nominal composition of Fe-1.5wt%Cr - 0.2wt% and mixture of Astaloy CrL with 0.5wt % natural graphite additions prepared in a Turbula mixer.

Distribution and morphology of internal and surface oxides of powder particles before and after sintering have been studied on a cross section of powder particles. It was performed by optical spectroscopy Olympus GX 71, scanning electron microscopy JEOL JSM 7000 F and TESLA BS 340. Composition of oxides was performed by EDX, using a LINC INCA system.

About 5g of powder and powder mixture was sintered in a quartz container in a laboratory tube furnace "MARSH" at 1120°C and 1200°C for 15 minutes.

The sintering experiment was carried out under flowing atmosphere of 10% H_2 /90% N_2 at flow rate of 4l/min. The input dew-point was -50°C. The sintering cycles were performed at constant heating rate of 50°C/min up to the sintering temperature with a 15 min soaking time. After sintering the specimens were cooled at 50°C/min down to 200°C.

Analyses of oxygen and carbon content were performed using LECO TC - 336 instruments.

3. Results and discussion

Theoretical thermodynamic calculations of required atmosphere composition were carried out during the sintering of Fe-Cr-C system in nitrogen/hydrogen atmosphere, paying special attention to carbothermal reduction process. In these calculations carbon was considered as pure non-dissolved graphite. According to these considerations, activity of carbon and surface oxides can be taken as 1.

If Cr_2O_3 is to be reduced by solid carbon, we can calculate the maximum pressures of active gases, which can be tolerated in the system considering free enthalpy changes ΔG^0 at absolute temperature T.

Since $\Delta G_T^0 = \Delta H - T\Delta S$ and $\Delta G_T^0 = -RT \ln K_p$ the Gibbs free energy changes ΔG^0 and the equilibrium constant K_p can be easily obtained from the HSC Chemistry 6.0 database.

For the reduction of Cr_2O_3 by graphite, the following reactions have to be considered:



If sintering is performed in 10% H_2 /90% N_2 the following reaction can occur:



The required composition of sintering atmosphere for oxide reduction during sintering at 1120°C and 1200°C is given in Table 1

Table 1 Required composition of sintering atmosphere at 1120°C and 1200°C

	P(CO) kPa	P(CO ₂) kPa	p(O ₂) kPa	P(H ₂ O) kPa	DP (°C)
1120 °C	13.7802	3.4278*10 ⁻³	4.7714*10 ⁻¹⁸	5.5161*10 ⁻³	-45
1200 °C	42.2042	1.7813*10 ⁻²	1.3426*10 ⁻¹⁶	9.8873*10 ⁻³	-38

Two types of oxides are present in Astaloy CrL. Surface oxides related to the surface of powder particles and internal oxides within the powder particles. Karlsson et al.[6] reported that the powder particles of chromium pre-alloyed powders are covered by a heterogeneous oxide layer consisting of continuous iron oxides layer with the thickness of above 5-7nm and particulate compounds with size of above 20-100nm with high content of strong oxide forming elements such as Cr, Mn and Si. Observations under the SEM of Astaloy CrL particles surfaces confirmed the presence of particulate oxides. Qualitative EDX analysis indicates that these particulate compounds are complex Fe-Mn-Cr-AL-Si-O oxide, Fig.1. These oxides are much more critical, because they cannot be reduced during sintering in normal conditions.

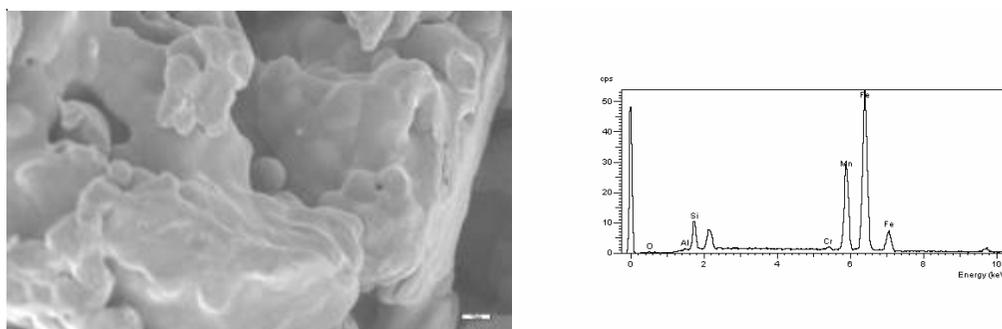


Fig.1 SEM+EDX analysis of particulate oxides on the surface of powder particles of Astaloy CrL

Observation of cross section of particles of received powders revealed that powder particles of Astaloy CrL contain relatively high amount of internal oxides, Fig.2. These oxides are small, individual and quite spherical particles with size of 0.5-3µm and are very often connected like „chains“ or form relatively large aggregates up to about 10µm long. The chemical composition of these oxides is mainly constituted by chromium and manganese, Fig.3.

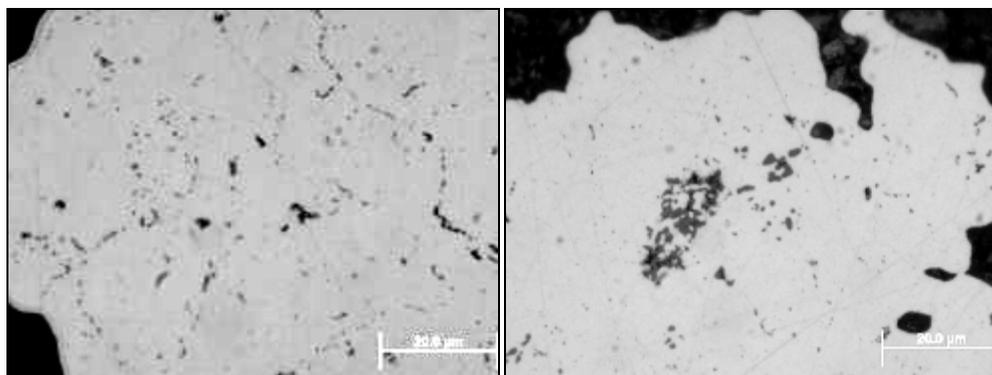


Fig.2 Non etched microstructure of powder particles of Astaloy CrL

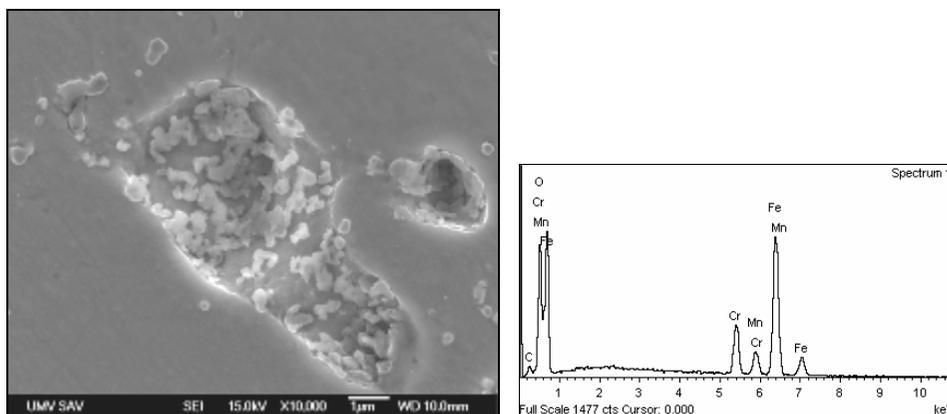


Fig.3 SEM+ EDX analysis of the oxides particles within the particles of Astaloy CrL

As mentioned above, an adequate reduction must be ensured during sintering in order to encourage neck formation.

The oxide reduction during sintering of Astaloy CrL is the result of combined action of admixed carbon and oxygen potential of the sintering atmosphere. The thermodynamically less stable layer of iron oxides is easily reduced by hydrogen from sintering atmosphere. Carbon is less effective than hydrogen at lower temperatures, but at temperature higher than 720°C the reduction activity of carbon increases and it begins to play a dominant role in the reduction process. The graphite reacts with oxygen from any source and the mixture of CO/CO₂ is formed during the carbothermal reduction of metallic oxides. The gas mixture is more reducing as the CO level in the mixture is higher. As expected, these conditions are more satisfyingly fulfilled as the temperature increases.

The oxygen content of material after sintering is strongly influenced by the temperature and the presence of carbon, Table 2.

Table 2 The change of powder weight, content of C and O before and after sintering

Material	Temperature	$\Delta m(\%)$	C wt% before sintering	C wt% after sintering	O wt% before sintering	O wt% after sintering
Astaloy CrL	1120°C	+0.94	0	0	0.14	0.155
	1200°C	+0.10	0	0	0.14	0.153
AstaloyCrL+0.5C	1120°C	-0.33	0.5	0.46	0.14	0.087
	1200°C	-0.23	0.5	0.39	0.14	0.034

By comparing the oxygen content, see Table 2, and observing the micrographs as polished microstructures, Fig.4a, it can be deduced, that sintering at 1120°C without carbon is not sufficient for oxides reduction.

The reduction is more effective at the higher temperature 1200°C, Fig.4b. The increase in oxygen content for sintering without carbon at both temperatures is related to the oxidation that takes place during cooling from the sintering zone.

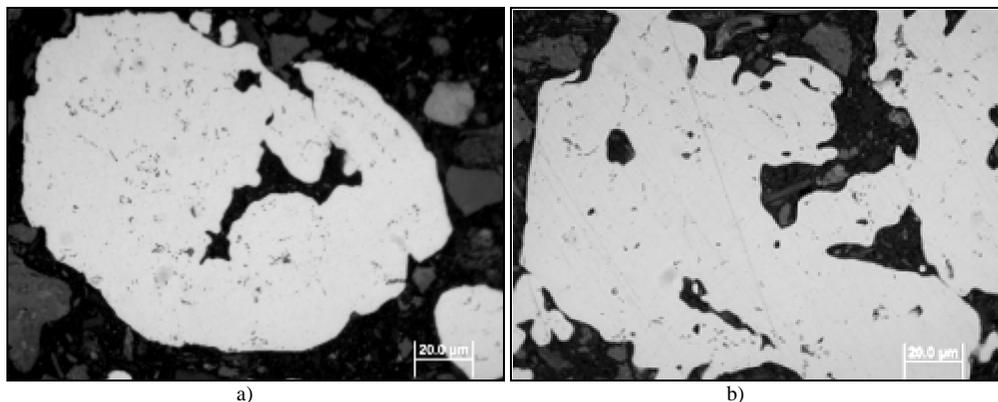


Fig.4 LOM micrographs of Astaloy CrL sintered at a) 1120°C b) 1200°C

Admixed carbon plays very important role in the reduction of oxides. The chemical analysis showed that oxygen level after sintering with carbon decreased. This reduction in oxygen and carbon content is caused by carbothermal reduction.

In the microstructure of Astaloy CrL powder particles sintered with carbon added at temperature of 1200°C presence of inner oxides wasn't observed, Fig.5b, in contrast with all the cases, when Astaloy CrL particles were sintered at 1120°C, Fig.5a. The reduction is more effective at higher sintering temperature.

These results are in a good agreement with experiments performed by Danninger et al. [9-11].

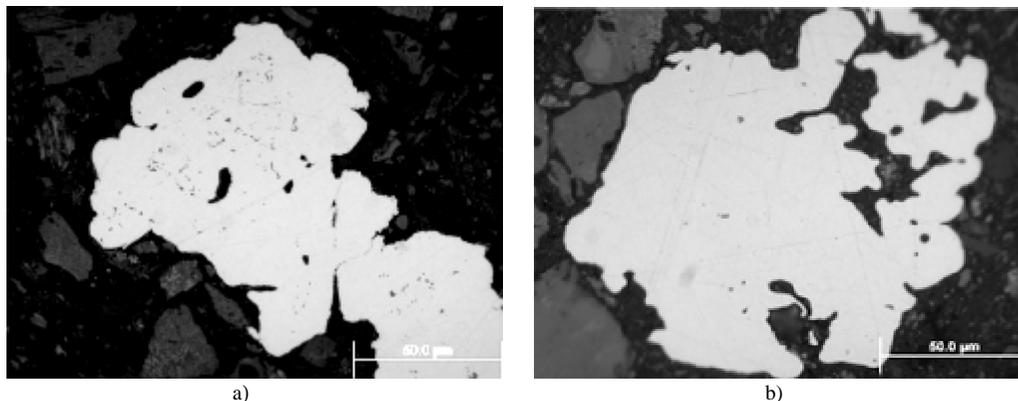


Fig.5 LOM micrographs of Astaloy CrL+0.5C sintered at a) 1120°C ... b) 1200°C

4. Conclusion

Thermodynamic calculations were carried out for reduction of Cr_2O_3 by solid carbon during sintering at 1120°C and 1200°C respectively.

Two types of oxides are present in Astaloy CrL, surface and internal oxides. Surface oxides are thermodynamically stable Fe-Mn-Cr-AL-Si-O compounds, internal oxides are Fe-Mn-Cr-O compounds.

Results confirm the key role of graphite addition for reduction of oxides during sintering the steels alloyed elements with high oxygen affinity.

The reduction of oxides is more effective at higher temperature. During sintering at 1200°C about 80% of all oxygen is removed while at 1120°C it is about 40%.

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